ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PREPARATION OF CHITOSAN-ZEOLITE COMPOSITES FOR ADSORPTION OF TEXTILE DYES AND ANALYSES OF ADSORPTION KINETICS

M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

TEKSTİL BOYALARININ ADSORPSİYONU İÇİN ÇİTOSAN-ZEOLİT KOMPOZİTLERİN HAZIRLANMASI VE ADSORPSİYON KİNETİĞİNİN İNCELENMESİ

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MAYIS 2014

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FOREWORD

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ABBREVIATIONS

AMPS	**:** 2-Acrylamido-2-methylpropane sulfonic acid
BET	**:** Brunauer, Emmet, and Teller
CEC	**:** Cation Exchange Capacity
EDTA	**:** Ethylenediaminetetraacetic acid
Eq.	**:** Equation
FTIR	**:** Fourier Transform Infrared Spectroscopy
NOM	**:** Natural Organic Matter
PVC	**:** Poly(vinyl chloride)
SEM	**:** Scanning Electron Microscope
TEM	**:** Transmission Electron Microscope
UF	**:** Urea-formaldehyde
UV	**:** Ultra-violet

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PREPARATION OF CHITOSAN-ZEOLITE COMPOSITES FOR ADSORPTION OF TEXTILE DYES AND ANALYSES OF ADSORPTION KINETICS

SUMMARY

There are many studies in literature using modified or pure chitosan that aims for adsorption of dye molecules, detoxification of water and wastewater, and color removal.

Some natural polymers are used for adsorption experiments and one of them is chitosan. Chitosan is a natural polymer, which is obtained from marine animals and fungies. Zeolite is a kind of clay, which is also used for adsorption, cheap and eases to form composite films.

The objection of this study was adsorption of textile dyes by chitosan derivatives. The derivations of chitosan were performed by mixing chitosan and zeolite solutions with magnetic stirrer, pouring the viscous solution onto Petri dishes to obtain 0.1 mm thick films when they are dried. Urea and formaldehyde were used to obtain crosslinked structure in different fractions to improve the characteristics of the composite. Highly crosslinked structure were used as gel for adsorption experiments.

Dye solutions are prepared in distilled water. The chitosan-zeolite composite films and gel were added to each dye solution (Reactive Blue 221, Reactive Red 195, Reactive Yellow 145 and Reactive Black 5). The experiments were repeated in different pH values and temperatures and different input ratios.

UV analysis was performed for the observation of color change in solutions and adsorption capacities are determined. The validations of the syntheses were obtained by FT-IR analyses. The structure of the composites were examined by SEM analyses. According to UV analysis results we could find adsorption capacities and adsorption kinetics of each composite for each dye in different conditions and had information about the behavior of the composites. FT-IR and SEM gave information about the structure of the composites prepared.

In this study, adsorption of textile dyes bu using chitosan-zeolite composites were examined and the effect of urea-formaldehyde crosslinking were observed. Adsorption at low temperatures were better than the others which shows that adsorption of textile dyes with chitosan-zeolite composites is exothermic. Adsorption was faster at pH 4 in short time which would be good for industrial cases while adsorption was more effective at pH 6 at the end of the experiments. Urea-formaldehyde improved physical and chemical characteristics of the composite.

TEKSTİL BOYALARININ ADSORPSİYONU İÇİN ÇİTOSAN-ZEOLİT KOMPOZİTLERİN HAZIRLANMASI VE ADSORPSİYON KİNETİĞİNİN İNCELENMESİ

ÖZET

Son dönemlerde çitosanın tekstil atık sularında adsorban olarak kullanımını inceleyen birçok makale yayınlanmıştır. Çitosan karides gibi bazı deniz canlıları ve mantarlardan elde edilir. Gıda endüstrisinin bir atığı olan karides kabuklarının bu iş için kullanılabilir duruma getirilmesi çevreci bir girişimdir. Bu tür çalışmalarda çitosanın tercih edilmesinin diğer bir nedeni ise çokça bulunduğu için ucuz olması ve adsorpsiyon için kullanılan petrokimya ürünü diğer adsorbanlara göre daha doğa dostu bir malzeme olmasıdır.

Bir çok kil üzerinde adsorpsiyon çalışmaları yürütülmektedir. Bunlardan biri de zeolittir. Zeolitler, üç boyutlu kristal yapılara sahip alkali ve toprak alkali metalleri içeren hidratlı alüminosilikatlardır. Zeolit gibi bazı killerin de adsorpsiyonda etkin olduklarını gösteren bazı makaleler yayınlanmıştır. Zeolit türevleri çitosana oranla çok daha ucuz bir malzemedir ancak adsorpsiyon kapasitesi de çitosana nazaran bir hayli düşüktür. Zeolit aynı zamanda da çitosanın film oluşturmasına da yardımcı olmaktadır.

Tekstil boyalarının doğaya zararlı olduğu herkes tarafından bilinir. Renklendirme amacıyla kullanılan birçok madde canlı yaşamını olumsuz etkilemektedir. Tekstilde kullanılan doğaya zarar verici kimyasallar bularla da sınırlı değildir. Boyaların atık sulardan adsorplanması ancak bunun bir kısmını oluşturur ve iyi bir arıtma olmaksızın salınan bu boyaların birçoğunun yarılanma ömrü onyıllar alır. Tekstil endüstrisinde kirletilen suyun büyük kısmını içilebilir su oluşturur ve birçok ülke de bu açıdan yoksundur. Bu nedenle de suyun geri kazanılarak tekrar kullanılması beklenir.

Tekstil atık suyu arıtma metodları genel olarak biyolojik, kimyasal ve fiziksel metodların bir kombinasyonu ile oluşturulur. Tekstil şirketleri suyun dışındaki değer kimyasalları da tekrar kullanmak isteyebilirler ve bunun için kendilerine en uygun proses kombinasyonunu suyun arıtılması işleminde oluşturabilirler. Bu sayede üretim ekonomisi düzenlenmiş olur. Yaptığımız çalışmanın ürünleri de bu kombinasyonlara entegre edilerek optimizasyonu sağlanabilir ve malzemenin seçici özellikleri göz önüne alınarak istenilen sonuçlar elde edilebilir.

Adsorpsiyon sulu çözeltiler için etkili bir saflaştırma metodudur. Birçok malzemenin boya adsorpsiyonundaki etkinlikleri incelenmiştir ve ekonomik şartlar da göz önünde bulundurularak sanayide kullanıma elverişli hale getirilmeye çalışılmıştır. Bunlardan biri de çitinin bir modifiye türevi olan ve biyolojik olarak doğada yok olabilen, doğaya uyum sağlayan, toksik olmayan, azot içeren lineer homopolimer bir polisakkarit olan çitosandır.

Bu çalışmayla tekstil boyalarının çitosan türevleri tarafından adsorpsiyonunun incelenmesi amaçlandı. Bunu yaparken de kompozit bileşiminde zeolit kullanımına karar verildi. Öncelikle çitosan ve zeolitin asitli suda ayrı ayrı çözeltileri oluşturuldu ve çözeltiler kompozit karışımını oluşturabilmek için, magnetik karıştırıcı yardımı ile uygun sıcaklıkta karıştırıldı. Elde edilen kompozit karışım Petri kaplarına dökülerek oda sıcaklığında kurumaya bırakıldı.

Sonuç olarak ortalama 10-20 μm kalınlığında kompozit filmler elde edildi. Aynı işlemler karışımdaki zeolit miktarını değiştirerek ve farklı üre-formaldehit oranlarıyla 75 °C sıcaklıkta çarpraz bağlanma yapılarak yeniden gerçekleştirildi ve aynı koşullarda kurutma yapılarak aynı kalınlıkta filmler elde edildi ancak yüksek oranda çarpraz bağlanmanın olduğu sentez jel olarak adsorpsiyon deneylerinde kullanıldı.

Üre ve formaldehit kullanılarak çapraz bağlanmış yapılar oluşturuldu ve böylece malzemenin adsorpsiyon özelliklerindeki değişimler gözlemlendi. Bunun yanısıra malzemenin fiziksel özelliklerinde de değişimler gerçekleşti. Farklı fraksiyonlarda kullanılan üre-formaldehit miktarları farklı özellikler gösterdiler. Yüksek oranda üre-formaldehit çağrazbağlı yapı içeren kompozit film yapılmaksızın jel olarak adsorpsiyon deneylerinde kullanıldı.

Çalışmada kullanılmak istenen boya çözeltileri (Reaktif Mavi 221, Reaktif Kırmızı 195, Reaktif Sarı 145 ve Reaktif Siyah 5) saf suda hazırlandı ve içlerine adsorpsiyon çalışmaları için hazırlanmış kompozitlerden çitosan miktarınca aynı oranlarda eklendi. Farklı sıcaklıklarda ve pHlarda adsorpsiyon yapılıp numuneler alınarak UV spektrofotometre yardımıyla adsorplanan boya miktarları hesaplanarak kompozitlerin etkinliği görüldü ve uygun sıcaklık ve pH değerlerine ulaşıldı. En iyi adsorpsiyon sonucu veren kompozitler için 1 günlük deney yapılarak endüstriye daha uygun olması beklenen konsantrasyon-adsorban miktarı hakkında bilgi sahibi olmaya çalışıldı.

UV sonuçlarından elde edilen veriler sayesinde adsorpsiyon kapasitelerine ve adsorpsiyon hız sabitlerine ulaşıldı. Böylelikle karşılaştırmalar daha kolayca yapılabildi ve çalışmada ilerlenebildi. Boya konsantrasyonlarındaki değişim nitel olarak da gözlemlenebildi. Çalışmalar yürütülürken malzemelerin farklı pH değerlerinde ve sıcaklıklarda farklı davranışlar gösterdiği görüldü. Bu özellikler farklı boyalar için benzer şekilde değiştiler.

Çalışmalarda kullanılan girdiler ve elde edilen kompozitler FTIR spektroskopisi ile incelenerek yapısal değişimler hakkında bilgi edinildi ve elde edilen analiz sonuçları neticesinde amaçlanan yapının elde edildiği sonucuna ulaşıldı. SEM (Taramalı elektron mikroskobu) ile de kompozitlerin morfolojileri incelendi. Böylelikle por boyutu, yüzey alanı, film kalınlığı gibi sentez ürünümüzü tanımamızı sağlayacak bilgiler elde edilerek malzemelerin bazı kimyasal ve fiziksel karakterizasyonlar yapılmış oldu.

Farklı boyalar kullanılmış olsa da adsorpsiyon sırasında benzer özellikler gözlendi. Adsorpsiyonun pH 4'te, oda sıcaklığında, düşük kil oranı ve yüksek çarprazbağlanma ile kısa sürede en iyi sonuçları verdiği gözlemlendi. Ancak uzun süreli adsorpsiyonda en iyi sonuçların pH 6 değerinde alındığı görüldü. Bu da Asitlik-bazlık değerlerinin adsorpsiyon kapasitesini ve hızını çok etkilendiğini göstermiş oldu. 35°C ve 50°C sıcaklıklarında yapılan çalışmalarda alınan sonuçlar, sıcaklık arttıkça adsorpsiyonun kötüleştiğini gösterdi.

Hazırlanan kompozitler ve boyalar arasındaki adsorplanmanın ekzotermik olduğunu göstermektedir. Çarpraz bağlanmanın kompozitin sulu ortamlardaki fiziksel özelliklerini iyileştirdiği nitel olarak gözlemlendi. Asitli çözeltilerde çözünen çitosanın asitli ortamlardaki kullanımları için daha uygun hale getirilmiş oldu ve olası bozunmalar engellenmiş oldu.

Sonuç olarak hazırlanan filmler ve yüksek oranda çarpraz bağlanmış çitosan/zeolit kompozit jelin iyi adsorpsiyon özelliklerinin olduğu gözlemlendi ancak en iyi kompozitin hangisi olduğuna, uygulama alanları ve ekonomileri ile ilgili optimizasyonları yapılarak karar verilebileceğine kanaatine varıldı. Bu durumun göz ardı edildiğinde yüksek oranda çarpraz bağlanmış kompozit jelin, yüzey alanı ve difüzyon avantajları göz önüne alındığında hızlı bir adsorpsiyon için en uygun sentez olduğu söylenebilir.

1. INTRODUCTION

In recent years, the world became much more sensitive about the environmental issues. This results with the need of environment friendly innovations in science. Because, the use of the chemicals which have bad influences to the environment increased for industries such as textile industry. With the increased demand for textile products, the textile industry and its wastewaters have been increasing proportionally, making it one of the main sources of severe pollution problems worldwide.

Dyes are among the unwanted textile wastewater contaminants and they are not only unwanted because of their colour but also because they are harmful to living organisms. Without a good treatment these dyes are stable and can remain in the environment for a long period of time. For instance, the half-life of hydrolysed Reactive Blue 19 is about 46 years at pH 7 and 25 °C [1]. The water used is generally a part of potable water which is scarce in many countries so recycling is highly recommended for decreasing the water requirements.

Textile wastewater treatment methods are generally a combination of biological, physical and chemical methods like coagulation/flocculation, electrochemical oxidation, activated carbon adsorption, reverse osmosis, ozone and oxidative/reductive chemical processes etc. and the textile company may also want to reuse some other chemicals in the wastewater and they have to optimize a suitable process combination for recovering wanted chemicals with water.

Adsorption is recognized as an effective process in aqueous solutions. A number of materials have been studied in the past in terms of efficiency for dye adsorption as well as economic viability. One of these is the chitosan, a natural polymer which is obtained from waste of seafood processing industry and chitosan was just a waste by-product before. This material is now being utilized by industry to solve problems and to improve existing products, as well as to create new ones. Chitosan is modified natural, biodegradable, biocompatible, non-toxic, as well as linear nitrogenous

polysaccharides, a basic polysaccharide homo-polymer [2]. Another material used for adsorption is zeolite, which is a low-cost, eco-friendly and accessible clay through its rich resources [3].

In this study, different compositions of chitosan/zeolite composite films were prepared and examined in synthetic dye solutions. Urea and formaldehyde were used as crosslinking agent to obtain resistant films to acidic/alkali solutions and improve the adsorption capacity of the composite.

2. THEORETICAL PART

2.1 Chitosan

Chitosan is a derivative of chitin, which is a biopolymer, has crustacean origin having structural similarity to cellulose. Chitin and chitosan are amino polysaccharides having amide/amino functionality and hydroxyl groups that can undergo chemical modifications to give a variety of materials in a number of applications in healthcare/biomedicine, biotechnology, water treatment, cosmetics and toiletries, food and beverages, agrochemicals, pulp and paper, textile finishes, photography products, product separation and recovery, membranes and other miscellaneous [4-13].

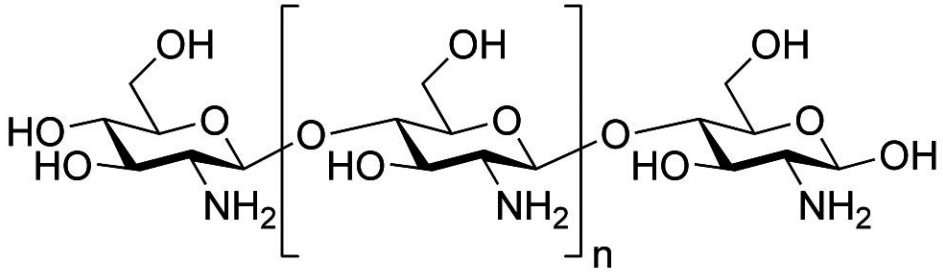


Figure 2.1 : The structure of chitosan

Their applications depend on their excellent adhesion characteristics, biocompatibility and admirable biodegradability with ecological safety and low toxicity with versatile biological activities such as antimicrobial activity and low immunogenicity [4-8]. Chitin is one of the most abundant polysaccharides (next only to cellulose) found in nature, making chitosan a plentiful and relatively inexpensive product. Coupled with the possibility of preparing a variety of chemically and enzymatically modified products and processes, these biopolymers having the rare amino functionality and two hydroxyl groups for chemical modifications are potential materials in a variety of applications in biomedical, biotechnological and pharmaceutical areas [9-15]. Despite its huge annual production and easy availability, chitin remains under the utilized resource primarily because of its

intractable molecular structure. However, chitosan derived from chitin because of its improved solubility and enhanced functionality is better placed for a variety of applications. The promise for this biomaterial is vast and will continue to increase as the chemistry to extend its capabilities and new applications are investigated [16].

Recent findings that chitosan is a good candidate as a support material for gene delivery [17], cell culture [18], and tissue engineering [19, 20] indicates its potential as novel functional materials. The main advantages of chitosan sorbents are their nontoxicity, high efficiency, biodegradability and low cost. Chitosan possesses various functional groups in its structure such as amine, hydroxyl and acetamide group that can be involved in sorption process [21]. However, chitosan still has some drawbacks such as lower stability that is a result of its hydrophillicity nature and pH sensitivity.

2.2 Zeolite

Zeolites are crystalline, hydrated aluminosilicates of alkali and earth metals that possess infinite, three-dimensional crystal structures. Made of a special crystalline structure that is porous but remains rigid in the presence of water, zeolite can be adapted for a variety of use such as household odor control products, water and waste water treatment and so on [22,23].

There are more than 50 different available types of aluminosilicate zeolites with pore openings ranging from less than 5 Å to larger than 10 Å. These porous, crystalline, hydrated aluminosilicates of alkali and alkaline earth cations possess a three dimensional structure. The negative charge created by the substitution of an AlO_4 tetrahedron for a SiO_4 tetrahedron is balanced by exchangeable cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}), which are located in large structural channels and cavities throughout the structure. These cations play a very important role in determining the adsorption and gas-separation properties of zeolites. These properties depend heavily on the size, charge density, and distribution of cations in the porous structure. These natural minerals are found with a Si/Al ratio ranging between 3 and 5 [24].

Along with quartz and feldspar, zeolites are “tektosilicates” that is, they consist of three-dimensional frameworks of silicon-oxygen $(SiO_4)^4$ tetrahedral wherein all four

corner oxygen atoms of each tetrahedron are shared with adjacent tetrahedral. The vast 3-dimensional networks are a result of all four corners for the tetrahedron being shared, producing low-density micro-porous materials.

Elements or cations within the first set of parentheses in the formula are known as exchangeable cations; those within the second set of parentheses are called structural cations, because with oxygen they make up the tetrahedral framework of the structure. Loosely bound molecular water is also present in the structures of all natural zeolites, surrounding the exchangeable cations in large pore spaces.

Table 2.1 : Sample Zeolite Formulas [25]

Mineral Name	General Formula
Analcime	$Na_{16}[Al_{16}Si_{32}O_{96}]\cdot 16H_2O$
Chabazite	$(Ca_{0.5},Na,K)_4[Al_4Si_8O_{24}]\cdot 12H_2O$
Clinoptilolite	$(Na,K)6[Al_6Si_30O_{72}]\cdot 20H_2O$
Erionite	$K_2(Na,Ca_{0.5})_8[Al_{10}Si_{26}O_{72}]\cdot 28H_2O$
Heulandite	$(Na,K)Ca_4[Al_9Si_{27}O_{72}]\cdot 24H_2O$
Laumontite	$Ca_4[Al_8Si_{16}O_{48}]\cdot 18H_2O$
Mesolite	$Na_{16}Ca_{16}[Al_{48}Si_{72}O_{240}]\cdot 64H_2O$
Scolecite	$Ca_8[Al_{16}Si_{24}O_{80}]\cdot 24H_2O$
Stilbite	$NaCa_4[Al_9Si_{27}O_{72}]\cdot 30H_2O$

The empirical formula of a zeolite is shown as:

$M_{2/n}O \cdot Al_2O_a \cdot xSiO_2 \bullet yH_2O$

M: any alkali or alkaline earth element,

n: the valence charge on that element,

x: a number from 2 to 10,

y: a number from 2 to 7.

The empirical and unit-cell formula of clinoptilolite, the most common of the natural zeolites, is:

$(Na,K)_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 6H_2O$ or $(Na_4K_4)(Al_8Si_{40})O_{96} \cdot 24H_2O$

2.3 Urea-formaldehyde

Urea-formaldehyde (UF) resins are formed by the reaction of urea and formaldehyde. UF resins are the main binders for wood composite boards, such as particleboards, fibreboards, or hardwood plywood [26]. In the use of UF resins, water solubility, good adhesion, high curing rate, and low cost are the attractive properties. Their drawbacks are low water resistance and emission of formaldehyde from wood boards, resulting from the low stability of the amino-methylene bond. The key parameter in the decrease of formaldehyde emission is lowering the formaldehyde/urea (F/U) ratio in the synthesis of UF resins. This leads to a reduction in the content of crosslinking groups in cured UF resins, lowering the strength and water resistance of adhesive joints in boards [27].

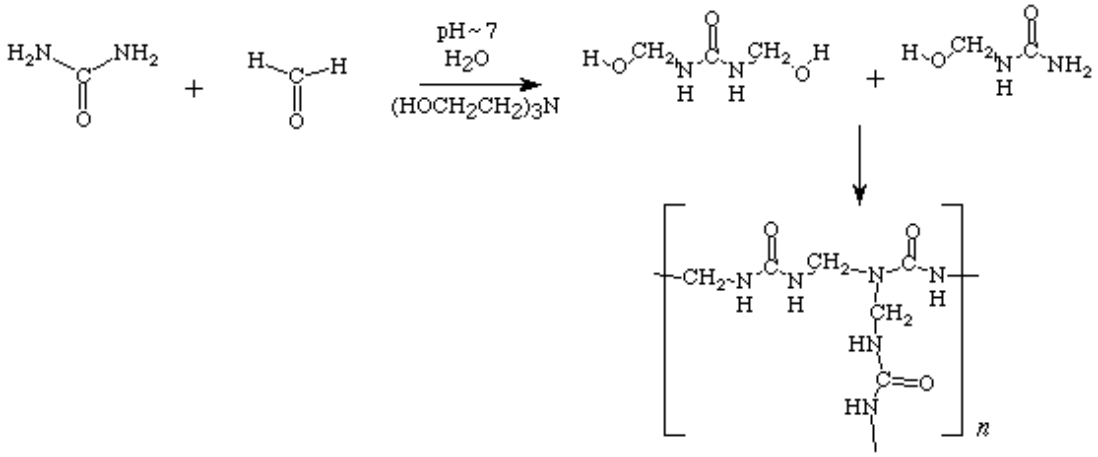


Figure 2.2 : Urea-formaldehyde polymer synthesis

2.4 Wastewater of Textile Industry and Its Treatment

In the production, there are several different steps generate highly contaminated liquid streams. The quantity of the concentration of the waste depend on different factors like the type of the processed fabric or the process itself. Type of machinery, chemicals applied and other characteristics of the processes determine the amount and composition of the generated wastewater. In the textile sector, although processes

should be considered separately, treatment of each process may not be considered individually.

Some processes in a textile mill hardly generate wastewater, such as yarn manufacture, weaving (some machines use water), and singeing (just some lightly polluted cooling water). The amount of wastewater produced in a process like sizing is small, but very concentrated. On the other hand, processes like scouring, bleaching and dyeing generate large amounts of wastewater, varying much in composition [28]. The average water consumption in textile process is 200-400L to process 1kg of finished product [29]. The reason is that textile industry is a chemically intensive industry. Textile finishing generates effulients containing significant amounts of a wide range of residues.

Table 2.2 : Some selected treatment processes for dyes and colour removal of industrial wastewater (I) [30-32]

Treatment methodology	Treatment Stage	Advantages	Limitations
Physico-chemical treatments			
Precipitation, Coagulation-flocculation	Pre/main treatment	Short detention time and low capital costs. Relatively good removal efficiencies.	Agglomerates separation and treatment. Selected operating condition.
Electrokinetic coagulation	Pre/main treatment	Economically feasible	High sludge production
Fenton process	Pre/main treatment	Effective for both soluble and insoluble coloured contaminants. No alternation in volume.	Sludge generation; problem with sludge disposal. Prohibitively expensive.
Ozonation	Main treatment	Effective for azo dye removal. Applied in gaseous state: no alteration of volume	Not suitable for dispersed dyes. Releases aromatic dyes. Short half-life of ozone (20 min)
Oxidation with NaOCl	Post treatment	Low temperature requirement. Initiates and	Cost intensive process. Release of

		accelerates azo bond cleavage	aromatic amines
Silica gels	Pre treatment	Effective for basic dyes	Side reactions prevent commercial application
Irradiation	Post treatment	Effective oxidation at lab scale	Requires a lot of dissolved oxygen (O2)
Photochemical process	Post treatment	No sludge production	Formation of by-products
Electrochemical oxidation	Pre treatment	No additional chemicals required and the end products are non-dangerous/hazardous.	Cost intensive process; mainly high cost of electricity
Ion exchange	Main treatment	Regeneration with low loss of adsorbents	Specific application; not effective for all dyes

Table 2.3 : Some selected treatment processes for dyes and colour removal of industrial wastewater (II) [30-32]

Treatment methodology	Treatment Stage	Advantages	Limitations
Adsorption with solid adsorbents such as:			
Activated carbon	Pre/post treatment	Economically attractive. Good removal efficiency of wide variety of dyes.	Very expensive. Intensive regeneration process
Peat	Pre treatment	Effective adsorbent due to cellular structure. No activation required.	Surface area is lower than activated carbon
Coal ashes	Pre treatment	Economically attractive. Good removal efficiency.	Larger contact times and huge quantities are required. Specific surface area for adsorption are lower than activated carbon
Wood chips/Wood sawdust	Pre treatment	Effective adsorbent due to cellular structure. Economically attractive. Good	Long retention times and huge quantities are required.

		adsorption capacity for acid dyes	
Biological treatments			
Aerobic process	Post treatment	Partial or complete decolourization for all classes of dyes	Expensive treatment
Anaerobic process	Main treatment	Resistant to wide variety of complex coloured compounds. Biogas produced is used for stream generation.	Longer acclimatization, phase
Single cell (Fungal, Algal & Bacterial)	Post treatment	Good removal efficiency for low volumes and concentrations. Very effective for specific color removal.	Culture maintenance is cost intensive. Cannot cope up with large volumes of WW.

Table 2.4 : Some selected treatment processes for dyes and colour removal of industrial wastewater (III) [30-32]

Treatment methodology	Treatment Stage	Advantages	Limitations
Emerging treatments			
Other advanced oxidation process	Main treatment	Complete mineralization ensured. Growing number of commercial applications. Effective pre-treatment methodology in integrated systems and enhances biodegradability.	Cost intensive process
Membrane filtration	Main treatment	Removes all dye types; recovery and reuse of chemicals and water.	High running cost. Concentrated sludge production. Dissolved solids are not separated in this process
Photocatalysis	Post treatment	Process carried out at ambient conditions. Inputs are no toxic and inexpensive. Complete mineralization with shorter detention times.	Effective for small amount of colored compounds. Expensive process.

Sonication	Pre treatment	Simplicity in use. Very effective in integrated systems.	Relatively new method and awaiting full-scale application.
Enzymatic treatment	Post treatment	Effective for specifically selected compounds. Unaffected by shock loadings and shorter contact times required.	Enzyme isolation and purification is tedious. Efficiency curtailed due to the presence of interferences.
Redox mediators	Pre/supportive Treatment	Easily available and enhances the process by increasing electron transfer efficiency	Concentration of redox mediator may give antagonistic effect. Also depends on biological activity of the system.
Engineered wetland systems	Pre/post treatment	Cost effective technology and can be operated with huge volumes of wastewater	High initial installation cost. Requires expertise and managing during monsoon becomes difficult

2.5 Dyes

Dyes as colored unsaturated organic molecules must have affinity for fibers to be effectively applied. The dyes on fibers are physically bound to the fiber by one or more physical forces including hydrogen bonding, Van der Waals, or ionic forces and in certain cases chemically bound by covalent bonds.

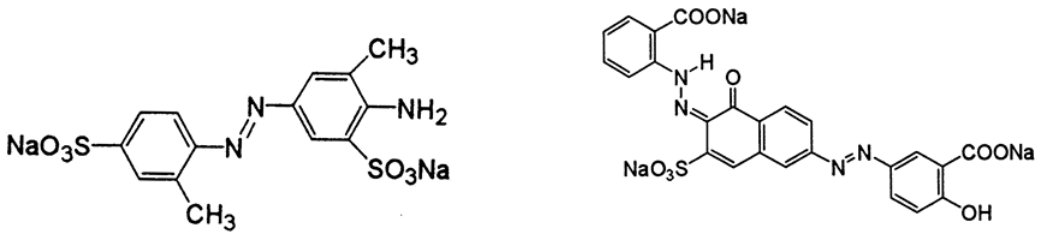
Dyes may be classified in a number of ways, including color, intended use, trade name, chemical constitution, and basis of application. Of these classification methods, chemical constitution and basis of application have been most widely used. Chemical constitution indicates the major chromophores present in the dye but does not indicate more than such structural aspects of the dye. A classification scheme for dyes has been developed and evolved for use by dyers, which is based on the method of application and to a lesser degree on the chemical constitution of the dye class. The classification scheme and major dye classes are outline below [33].

Table 2.5 : The classification of dyes

Dyes containing anionic funcional groups	Dyes need chemical reaction before
Acid dyes	Vat dyes
Direct dyes	Azoic dyes
Mordant dyes	Sulfur dyes
Reactive dyes	
Dyes containing cationic funcional groups	Special colorant classes
Basic dyes	Disperse dyes
	Solvent dyes
	Pigments
	Natural dyes

Acid Dyes: The acid dyes are large dyes containing one or more sulfonic or carboxylic acid salt functional groups. These dyes are dyed onto fibers from acid solution, since positive charge development within the fiber in acid solutions acts as

a driving force for dye diffusion and migration into the fiber. Acid Yellow 69 can be given as an example [34].

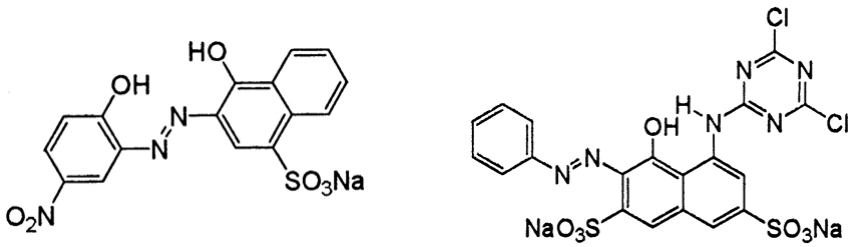


(a) (b)

Figure 2.3: (a) Acid Yellow 69, (b) Direct Red 185

Direct Dyes: Direct or substantive dyes are a special class of dyes that penetrate cellulosic fibers readily and have good affinity for these fibers due to their size and shape. Whereas acid dyes are large and bulky, direct dyes are long, narrow, and flat in molecular structure, which allows them to readily enter the cellulose structure and interact with the cellulose in such a way as to provide good fiber affinity. Direct dyes often contain one or more azo groups connecting aromatic chromophores, thereby providing a straight chain dye molecule. Since charge development is not a primary consideration in diffusion of direct dyes onto cellulosics, the dyes are usually applied from basic solutions in which cellulosics are more stable and more likely to swell. Direct Red 185 can be given as an example [34].

Mordant Dyes: Mordant dyes are acid dyes that have special sites other than acid salt anion groups that can react with a metal salt mordant. Mordant dyes are "tailor-made" to chelate with metal ions to form a strong organometallic complex of limited solubility and greater colorfastness. The fiber may be dyed initially and then mordanted (postmordanting), dyed and mordanted simultaneously (comordanting), or mordanted and then dyed (premordanting) . Of the three methods, postmordanting is preferred. Salts of chromium, aluminium, copper, iron, tin, and cobalt are commonly used as mordants. Since the mordant affects the electron distribution and density within the dye, the color of the dyed fabric tends to change. Mordant Brown 35 can be given as an example [34].

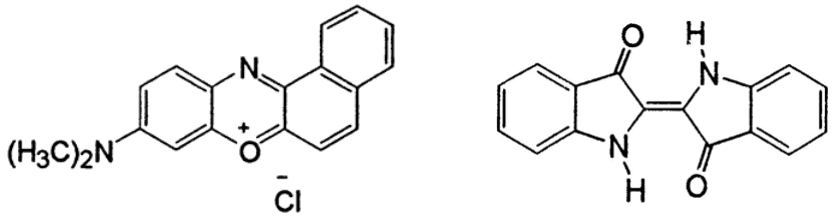


(a) (b)

Figure 2.4: (a) Mordant Brown 35, (b) Reactive Red 2

Reactive Dyes: Reactive dyes are dyes, which usually have the basic structure of acid, direct, or mo1rdant dyes but which in addition have a reactive group capable of covalent bond formation with the fiber. Since the fiber must have reasonable reactivity toward the dye reactive group, application of these dyes has been limited to cellulosic, protein, and nylon fibers for the most part [33]. Reactive Red 2 can be given as an example.

Basic Dyes: Basic or cationic dyes are colored cationic salts of amine derivatives. Basic dye cations will migrate toward negative charges inside the fiber. The dyes may be applied to cellulosic, protein, nylon, acrylic, and specially modified synthetic fibers. Although the dyes generally are of striking brilliance and intensity, the colorfastness of the dyes on cellulosic, protein, and nylon fibers is generally poor. Basic Blue 6 can be given as an example [34].

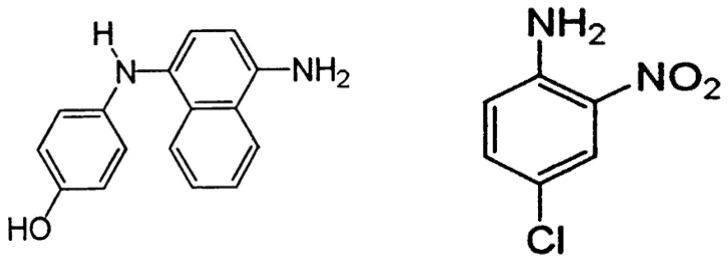


(a) (b)

Figure 2.5: (a) Basic Blue 6, (b) Vat Blue 1

Vat Dyes: Vat dyes are usually water-insoluble dyes that can be chemically reduced in the presence of base to form a water-soluble and colorless leuco form of the dye, which is then appl ied to the fiber. Vat dyes can be readily applied to cellulosic fibers and most synthetic fibers, but care must be taken in applying the dyes to protein fibers due to the high basicity of the leuco dye solution that can damage protein fibers [33]. Vat Blue 1 can be given as an example.

Sulphur Dyes: Sulphur dyes are inexpensive complex reaction mixtures of selected aromatic compounds with sodium polysulfide. The sulphur dyes are chemically reduced in the presence of base prior to application to the fiber, and are reoxidized after dyeing on the fiber by oxygen in the air or by application of a mild oxidizing agent such as hydrogen peroxide. Sulphur Green 6 can be given as an example [34].

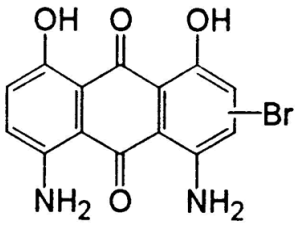


(a) (b)

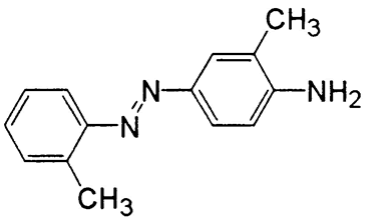
Figure 2.6: (a) Sulphur Green 6, (b) Azoic Diazo Component 9 (Orange)

Azoic Dyes: Azoic or naphthol dyes are formed in situ on the fabric through a coupling reaction of an aromatic alcohol or amine such as naphthol (the coupling component) with a diazonium salt (the diazo component). The fabric is usually impregnated first with the aromatic coupling component followed by immersion of the fabric in a solution containing the diazo component, with the azoic dye being formed instantaneously. Owing to the instability of the components, the dyeings are carried out near room temperature. The dyes have moderate fastness, and dyeings may be mordanted to increase fastness. Azoic Diazo Component 9 can be given as an example [34].

Disperse Dyes: Disperse dyes were formulated and introduced to permit dyeing of hydrophobic thermoplastic fibers including acetate, triacetate, nylon, polyester, acrylic, and other synthetics. The disperse dyes are small polar molecules, usually containing anthraquinone or azo groups, which do not have charged cationic or anionic groups within the structure. The disperse dyes are sparingly soluble in water and must be dispersed with aid of a surfactant in the dye bath. As the small amount of dissolved disperse dye diffuses into the fiber, additional dye dispersed in solution is dissolved, until the disperse dye is nearly completely exhausted onto the fiber. Disperse Blue 81 can be given as an example [34].



(a)

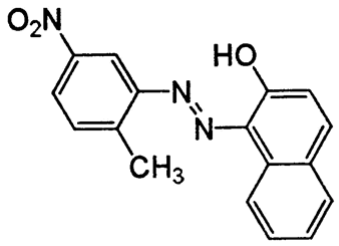


(b)

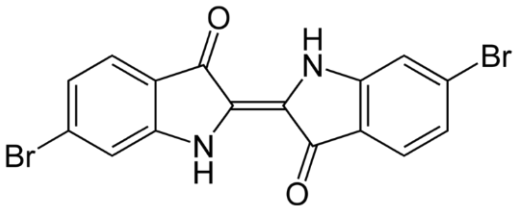
Figure 2.7: (a) Disperse Blue 81, (b) Solvent Yellow 3

Solvent Dyes: Solvent dyes often resemb1e dyes in other classes, except that these dyes contain groups that improve their solubility in solvents such as alcohols and chlorinated hydrocarbons. It is often possible with solvent dyes to dye certain fibers, which would be poorly dyeable from aqueous solution. Solvent Yellow 3 can be given as an example [34].

Pigments: Pigments as a class are colored materials that are insoluble in their medium of application. As a result, they cannot penetrate or become readily fixed to a fiber and must be "locked" onto the fiber surface by use of a polymeric adhesive binder that encapsulates and holds the pigment onto the fibers. Pigments include inorganic salts, insoluble azo or vat dyes, toners, lakes, metallic complexes, and organometallic complexes. Some binders are preformed water-insoluble polymers applied from solvents or as emulsions, whereas others are water-soluble or emulsifiable polymers which can be chemically crosslinked and insolubilized after application by drying and heating. The pigment-binder systems tend to stiffen textiles, and have moderate to poor fastness, since they are surface treatments. Pigment Orange 3 can be given as an example [34].



(a)



(b)

Figure 2.8: (a) Pigment Orange 3, (b) Tyrian Puple

Natural Dyes: Natural dyes and pigments are derived from mineral, animal, or plant sources and generally are complex mixtures of materials. A number of natural dyes can be classified as acid or vat dyes and can be readily mordanted. In general, the natural dyes give more muted tones than synthetic dyes and are useful only on natural or regenerated fibers. Tyrian Purple can be given as an example [34].

2.6 Adsorption

2.6.1 Definition of adsorption

Atoms, ions or molecules being adsorbed on a solid surface is called adsorption, when the adsorbed particles leave the surface, it is called desorption, the solid is called adsorbent and the substance adsorbed on the solid surface is called adsorbed substance. Adsorption occurs on the interface of two different phases such as liquid-liquid, gas-liquid, gas-solid, depending on the fact that the substance leaves one phase, cumulates and concentrates on the other [35].

Adsorption is realized primarily in 4 steps.

i) The adsorbed particles in gas or liquid is diffused towards the boundary of film layer, which coats the adsorbent.
ii) The adsorbed particles moves along to the pores of adsorbent.
iii) The adsorbed particles arrives to the surface by moving in the pores, where adsorption will occur.
iv) The adsorbed particles hold on to the pore surface of adsorbent.

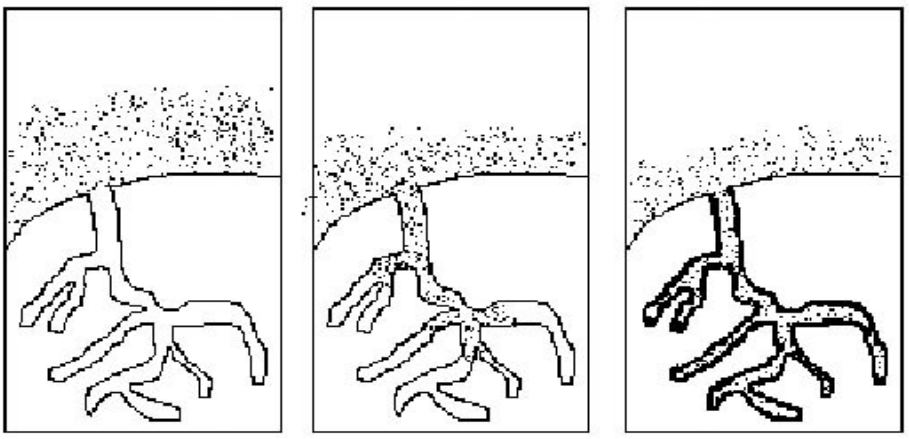


Figure 2.9: Adsorption Mechanism

2.6.2 Adsorption types

2.6.2.1 Physical adsorption

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through weak intermolecular interactions. Physisorption is generally considered as an effective method for quickly lowering the concentration of dissolved dyes in an effluent [36]. It is characterized by:

i) Low temperature, always under the critical temperature of the adsorbate

ii) Type of interaction: Intermolecular forces (Van der Waals forces)

iii) Low enthalpy: $\Delta H < 20$ kJ/mole

iv) Adsorption takes place in multilayer

v) Low activation energy

2.6.2.2 Chemical adsorption

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to physisorption [36]. It is characterized by:

i) High temperatures.

ii) Type of interaction: strong; covalent bond between adsorbate and surface.

iii) High enthalpy: $\Delta H \sim 400$ kJ/mole

iv) Adsorption takes place only in a monolayer.

v) High activation energy

Table 2.6 : Comparison between physical and chemical adsorption

Physical adsorption	Chemical adsorption
Molecular condensation in the capillaries.	Monomolecular layer of the adsorbate on the surface.
Without chemical bonding.	With chemical bonding.
Reversible can be desorption.	Non – reversible.
Nonselective surface attachment.	Selective surface attachment.

2.6.3 Factors affecting adsorption

The factors affecting the adsorption process are:

i) Surface area,
ii) Nature and initial concentration of adsorbate,
iii) Solution pH,
iv) Temperature,
v) Interfering substances,
vi) Nature and dose of adsorbent.

Since adsorption is a surface phenomenon, the extent of adsorption is proportional to the specific surface area that is defined as that portion of the total surface area that is available for adsorption [37, 38]. Thus more finely divided and more porous is the solid greater is the amount of adsorption accomplished per unit weight of a solid adsorbent [39]. The major contribution to surface area is located in the pores of molecular dimensions. For example, the surface area of several activated carbon used for wastewater treatment is about 1,000 m2/g, with a mean particle diameter of about 1.6 mm and density of 1.4 g/cm3. Assuming spherical particles, only about 0.0003% of the total surface is the external surface of the carbon particle [40].

The physicochemical nature of the adsorbent drastically affects both rate and capacity of adsorption. The solubility of the solute greatly influences the adsorption equilibrium. In general, an inverse relationship can be expected between the extent of adsorption of a solute and its solubility in the solvent where the adsorption takes place. Molecular size is also relevant as it relates to the rate of uptake of organic solutes through the porous of the adsorbent material if the rate is controlled by intraparticle transport. In this case the reaction will generally proceed more rapidly with decrease of adsorbate molecule [39, 41–43].

The pH of the solution affects the extent of adsorption because the distribution of surface charge of the adsorbent can change (because of the composition of raw materials and the technique of activation) thus varying the extent of adsorption according to the adsorbate functional groups [39, 44–46]. For example, Hamdaoui [47] showed that adsorption of methylene blue on sawdust and crushed brick increased by increasing pH (until a value of 9). For pH, lower than 5 both adsorbents

were positively charged: in this case, the adsorption decreased because methylene blue is a cationic dye.

Another important parameter is the temperature. Adsorption reactions are normally exothermic; thus, the extent of adsorption generally increases with decreasing temperature [39, 48–50].

Finally, the adsorption can be affected by the concentration of organic and inorganic compounds. The adsorption process is strongly influenced by a mixture of many compounds which are typically present in water and wastewater. The compounds can mutually enhance adsorption, may act relatively independently, or may interfere with one other. In most cases, as also shown hereinafter, natural organic matter (NOM) negatively affects the adsorption of emerging compounds in surface waters and wastewaters [46, 51, 52].

2.6.4 Adsorption capacity

In a solid–liquid system, adsorption results in the removal of solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase [53]. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm according to the general Eq. (2.1):

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad \textbf{(2.1)}$$

where q_t (mg/g) is the amount of adsorbate per mass unit of adsorbent at time *t*, C_0 and *Ct* (mg/L) are the initial and at time t concentration of adsorbate, respectively, *V* is the volume of the solution (L), and m is the mass of adsorbent (g).

2.6.5 Adsorption kinetics

Kinetic models are used to investigate the mechanism of sorption and rate controlling steps, which is helpful for selecting optimum operating conditions.

Pseudo-first order Langergren Equation [54]:

$$ln(q_e - q_t) = ln(q_e) - k_1 t \qquad \textbf{(2.2)}$$

Second-order rate equation [55]:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_t} + kt \quad \textbf{(2.3)}$$

Pseudo-second order equation [55]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \textbf{(2.4)}$$

q_e= Amount of dye adsorbed at equilibrium, (mg/g)

q_t= Amount of dye adsorbed at the time, (mg/g)

k_1= The rate constant of first order adsorption, (min^{-1})

k= The rate constant of first order adsorption, $(g/mg.min)$

k_2= The rate constant of pseudo-second order adsorption, $(g/mg.min)$

If the y values in the equations are added to graphic *t*, k_1, *k*, and k_2 values are found.

2.6.6 Adsorption studies of chitosan composites

Increase in the usage of adsorption method for wastewater purification and the increase of polymeric technologies increases the studies about developing adsorbents with different features of polymeric materials. The studies have been realized with much kind of organic and inorganic materials and recently there are many studies about polymeric materials. In some cases this materials are used together to be able to get more sophisticated materials. Many kind of chitosan composites are also prepared for different aims. Some of them are used for dye and heavy metal adsorption.

In a research, Babel S. and Kurniawan A.T. used low cost adsorbents such as chitosan and zeolite to adsorb heavy metals from wastewater instead of using activated carbon that is quite expensive on comparison. Chitosan was more effective on the adsorption of heavy metals then the cheaper material zeolite. In the research, both materials were used separately [56].

Another research is about chitosan-polyurethane composites that was done by Won, S. L., Lee, H. C., Jeong, Y. G., Min, B. G., and Lee, S. C. in 2009. This composite was used to adsorb Acid Violet 48. Lyoo, W. S., Lee, H. C., Jeong, Y. G., Min, B. G., and Lee, S. C. also worked on the same materials and found that that the adsorption capacity of neat polyurethane was comparably lower. This indicated that

the amine groups in the neat polyurethane could not react specifically as an active site to adsorb dye but it was a great matric material for immobilize chitosan polymer [57].

In 2004, Chang and Juang studied the chitosan/activated clay composites. They concluded that the addition of activated clay could enhance the ability of chitosan to agglomerate and improve the hardness of the beads based on the Stokes Laws. In the adsorption studies of methylene blue and reactive dye (RR22), the chitosan composites had a comparable adsorption in comparison to chitosan beads. [58]. Modified clays were also used to adsorb dyes and heavy metals [59, 60].

Wan Ngah, Ariff, and Hanafiah, prepared crosslinked chitosan/bentonite composites to adsorb tartrazine, a dye that contains azo group that is harmful to living things [61]. The chitosan composites, crosslinked with epichlorohydrin were able to improve the chitosan performance as an adsorbent [62]. A crosslinking agent can stabilize chitosan in acid solutions so that chitosan becomes insoluble. According to Wan Ngah, Ariff, and Hanafiah, the pH of the tartrazine plays a crucial role in the adsorption process. At lower pH, the surface of the adsorbent would carry positive charge and tartrazine molecules would be attracted. As pH increased, the surface of the adsorbent carried charges that are more negative. This would result in repulsion between tartrazine and the adsorbent.

In 2008, Hameed, B. H., Hasan, M., and Ahmad, A. L. prepared chitosan/palm oil beads to adsorb Reactive Blue 19. At lower pH, the adsorption capacity increased. At pH > 10, the adsorption capacity decreased tremendously due to the decrease in the total number and the diameter of the pores in chitosan beads. Crosslinking of the beads also caused decrease of adsorption capacity as it had difficulty for transferring the dye molecules [63].

Zhu, H. Y., Jiang, R., and Xiao, L. prepared Chitosan/kaolin/γ-Fe2O3 composite. They prepared the new chitosan beads by blending chitosan with maghemite (γ-Fe_2O_3) and kaolin. According to SEM and TEM images, it was found that there was many pores and pleats on the surface of the composite that provided active sites for the dyes. The composite adsorbed methyl orange up to 70% at pH 6. Addition of anions caused decreasing on adsorption of methyl orange [64].

Alumina is suitable to use as an adsorbent due to the amphoteric character of hydrous aluminium hydroxides. Few works have been carried out on the application of chitosan/ceramic alumina composites as an adsorbent to remove anionic and cationic heavy metals such as As(III), As(V) [65], Cr(VI) [66], Cu(II) and Ni(II) [67]. Oxalic acid is used in the process of forming the composites instead of the acetic acid because oxalic acid is a dicarboxylate and functions as a bridge between alumina and chitosan.

Chitosan/perlite composites have been applied as an adsorbent to remove heavy metals such as cadmium [68], chromium [69], and copper and nickel [70]. Shameem found that pure perlite and chitosan did not adsorb any cadmium at pH< 4. The composites showed two distinct regions in the pH curve. At pH between 2 and 4.5, mainly –NH2 groups in chitosan acted as active sites but at pH> 4.5, –OH groups became the active sites for cadmium adsorption. EDTA was used in desorption studies based on its strong chelating properties and it was found that almost 98% of the adsorbed Cd(II) ions were recovered in the first cycle [68].

Tran reported that hydrogel (2-acrylamido-2-methyl-1-propansulfonic acid, AMPS) cross-linked with chitosan matrix and magnetic particles were quite attractive for the removal of pollutants [71]. On the other hand, Huang prepared crosslinked chitosan-magnetite composites by using epichlorohydrin as the agent and found that modification crosslinking did not always reduce adsorption capacity [72]. Meanwhile, Liu investigated the removal efficiency of Pb(II), Cu(II) and Cd(II) from water and found that there was a decrease in magnetic saturation due to the increased mass of glutaraldehyde and chitosan on the surface of the magnetic nanoparticles. This magnetic property has strong magnetic response and can be separated easily from the solution with the help of external magnetic force. Ultrasound radiation was employed to disperse magnetic chitosan so that the magnetic chitosan composites and Pb(II) could interact efficiently and at a much faster rate [73].

Chitosan/cotton fiber composites had been prepared to remove Au(III)[74], Hg(II) [75], Pb(II), Ni(II), Cd(II) and Cu(II) [76]. Cotton fiber was treated with sodium periodate before being added into the chitosan solution in the preparation of composite beads. Based on kinetic studies, Zhang found that the rate-controlling step for Pb^{2+}, Ni^{2+} and Cd^{2+} was liquid film diffusion. For Cu^{2+}, the rate-controlling step was particle diffusion and it was found the adsorption rate was much compared to

Pb^{2+}, Ni^{2+} and Cd^{2+}. This was due to the interaction of Cu^{2+} with coordination atom was much faster than the other metal ions [76]. As a result, a copper complex matrix rapidly formed around the resin particle, which retarded the diffusion of metal ions into the interior part of resin particle. There was no significant difference in adsorption capacity between composite with Schiff base bond and C–N single bond [74, 75].

Sand can be modified to adsorb heavy metals and dyes in wastewater. Wan, Kan, Lin, Buenda, and Wu have reported on the application of chitosan immobilized on sand in the adsorption of Cu(II) [77]. Hatice, Parfait, Erdogan, and Sage showed that by coating clay particles with chitosan, the net surface charge of the clay has shifted from negative to positive and the pH_{PZC} has increased from 2.8 to 5.8 [78]. Chitosan/sand composites have shown better adsorption capacity than any of its component used alone. This is due to the three dimensional structure of the adsorbent used. Amine groups in chitosan provide active sites for the formation of complexes with metallic ions, which are stabilized by coordination. As the amount of acetyl groups in the structure increases, the maximum adsorption capacity of heavy metals decreases [77].

Cellulose, the most abundant and renewable biopolymer in nature is also one of the promising raw materials available for the preparation of various functional materials with better cost efficiency [79-82]. Some literatures reported on the use of cellulose immobilized on chitosan to form chitosan–cellulose composite beads. Sun reported that the adsorption capacity of dried chitosan biosorbent was nearly three times higher than that of freeze-dried chitosan composites, indicating the better stability of freeze-dried chitosan/cellulose composites [83]. Li and Bai reported that the crosslinking reaction improved the acid resistance of the composite beads and provided the evidence that some of the amine groups in chitosan were consumed or shielded by the crosslinking reactions, as indicated in zeta potential studies [84].

Fan produced chitosan coated montmorillonite for the removal of Cr(VI). Like other composites, the pH of the solution affects the adsorption capacity because chromium forms different kinds of anions at different pH values of the solution. Their kinetic results best fitted the pseudo second order model, indicating that the rate determining step involved chemisorption [85].

Chitosan was also immobilized by using poly(vinyl alcohol)(PVA) to form chitosan/PVA composites [86, 87]. This type of composite has been used to remove Cu(II) [86] and Cd(II) [87] from wastewater. The methods for the preparation of the composite beads are slightly different. In Kumar's work, the system temperature was raised to 90 ◦C in order to distill out some part of the water as an azeotropic mixture. Tween 80(polysorbate) was used in the preparation process as a non-ionic surfactant. It acted as an emulsifier during the preparation of droplets suspension. Desorption studies were carried out with more than 60% recovery, suggesting that the adsorbent was recyclable [86, 87]. Cu(II) kinetic data fitted well the pseudo second order model.

Poly(vinyl chloride)(PVC) has high surface area, good physical and chemical stabilities especially in concentrated acidic, basic media and organic solvents for a period of time. Furthermore, the surface of PVC can be modified by sorbent to obtain reversible and efficient enrichment of metal ions [88]. A biosorbent was developed by coating chitosan onto PVC beads. The composite beads were used to adsorb copper and nickel ions from aqueous solution. Similar to other composite beads, the pH of the solution has to be taken into consideration since complexion of the metal ions occurred at higher pH. The maximum adsorption capacities of chitosan/PVC composites were 87.9 and 120.5 mg/g for copper and nickel, respectively. The isotherm data were best described by Langmuir model [89].

Alginate is a water-soluble linear polysaccharide extracted from brown seaweed. The physical and chemical properties of alginates such as porosity and degradability can be easily modified in mild conditions. Wan Ngah and Fatinathan immobilized alginate on chitosan to form the composite beads to adsorb Cu(II). Based on desorption studies, the composite beads showed moderate performance since it recovered only 43% of heavy metal [90].

Most adsorption studies of heavy metals were conducted in an aqueous condition. However, Zhang introduced an experiment on the removal of mercury vapor (Hg^0) by chitosan/bentonite composites [91]. It was reported that chitosan/bentonite composites had a much lower surface area compared to bentonite. This could possibly be due to the blockage of micropores in bentonite after chemical modification. This resulted in a decrease in the amount of Hg^0 removed. In contrast, Yang and Chen found that chitosan/bentonite composites were a good adsorbent for

removing mercury ions from wastewater. Therefore, based on the above findings it can be concluded that the mechanisms of Hg^0 in the gas phase are completely different from that of mercury ions in aqueous condition. However, the detailed mechanisms of Hg^0 removal by chitosan/bentonite composites were not identified [92].

2.6.7 Clay-adsorbate interactions

Clays are important constituents of soil and have good ion exchange capacity; clay minerals take up various contaminants from water as it flows over soil or penetrates underground. The surface activity of clays depend on factors like chemical composition, nature of the surface atoms, the type and extent of defect sites, layer charge and the type of exchangeable cations, etc. [93]. The environmental role of clays is influenced by factors like pH, ionic strength, pressure and temperature of the surrounding medium [94]. The large surface area, cation exchange capacity (CEC), chemical and mechanical stability, layered structure, etc., determine the usefulness of the clays as a natural cleaning agent. Clays are known to possess both Brönsted and Lewis type of acidity and the acidic sites further enhance their adsorptive capacities for basic ions and groups [95].

It is observed that when the uptake of pollutants by the clays does not exceed the CEC, the mechanism of adsorption is dominated by ion exchange, but if the uptake is more than the CEC, the ions may be held through hydrophobic bonding [96]. The strength of such interactions are determined by the particular structural and related features of the clay. Clay-adsorbate interactions may proceed via Van der Waals type weak bonding, hydrophobic effects and even H-bonding, all of which are likely to play important roles in holding the pollutants to the clay surface. Crystal imperfections in the clay minerals may also affect adsorption and reaction processes on the clay surface [97].

Use of natural zeolites (and those modified by treating with acids and bases or surfactants) as adsorbents for water and wastewater treatment with respect to a variety of contaminants like ammonium, heavy metals, inorganic anions, dyes and humic substances has also been discussed recently [98].

3. EXPERIMENTAL

3.1 Chemicals Used

Chitosan was supplied from Sigma-Aldrich in the form of ground flakes and powder. Clinoptilolite-rich natural zeolite was used which was obtained from Gördes-Fındıcak (Manisa, Turkey). The manufacturing firm of zeolite was Esan. Urea was supplied from Carlo Erba. The formaldehyde solution (37%) used was obtained from Merck, acetic acid from Glacier and sodium hydroxide from Sigma-Aldrich. Dyes were supplied from Solar Fine Chemicals. Reactive Blue 221, Reactive Red 195, Reactive Black 5, Reactive Yellow 145 were used as adsorbate.

3.2 Equipment Used

Heidolph MR was used as heater and magnetic stirrer. This instrument can be heated to a maximum temperature of 350°C and its maximum stirrring rate is 1250 rpm.

The wavelengths of maximum absorbance was measured by the UV-visible spectrometer with the trademark Hitachi U-0080D, which is able to measure the wavelength from 200 nm to 1100 nm.

For the validations of the synthesis Fourier Transform Infrared Spectroscopy (FTIR) Spectrum 65 model with Perkin Elmer the trademark.

The trademark of the drying oven is Binder, which has maximum heating capacity 300°C and was used to dry the chitosan/zeolite composite films.

Philips trademark ESEM–FEG XL-30 was used for Scanning Electron Microscope (SEM) analyses to characterise the structure of the composites prepared.

3.3 Synthesis of Chitosan-Zeolite Composite Films

3.3.1 Synthesis of non-crosslinked chitosan-zeolite composite films

The composite films were prepared by mixing chitosan and zeolite solutions in water. Chitosan-zeolite ratio in mixtures were 5:2 and 5:4 (w/w). Firstly 1 g of chitosan was dissolved in 100 ml water and 2 ml of acetic acid with constant stirring for 30 minutes at 50°C. At the same 0.4 g of zeolite was dispersed in 100 ml water and 2 ml of acetic acid with constant stirring for 30 minutes at 50°C. These solutions were mixed and stirred for 30 min at the same temperature for a good mixing. Then the mixtures were cast on watch glasses and left for a couple of days to dry at room temperature. Obtained films were used for adsorption experiments. The same procedure was followed to obtain composite films with 5:4 chitosan-zeolite ratio.

3.3.2 Synthesis of crosslinked chitosan-zeolite composite films

The composite films were prepared by mixing chitosan and zeolite solutions in water. Zeolite and chitosan ratio in the mixtures were 40%. In three different beakers, 1 g of chitosan was dissolved in 100 ml water and 2 ml of acetic acid with constant stirring for 30 minutes at 50°C. In three different beakers, 0.4 g of zeolite was dispersed in 100 ml water and 2 ml of acetic acid with constant stirring for 30 minutes at 50°C. Each zeolite mixture was poured into each chitosan mixture and the temperature was increased up to 70°C.

2.4 g of urea was dissolved in 18 ml of formaldehyde solution (37%). Then 1/6 of the urea/formaldehyde mixture was added dropwise to one of the chitosan/zeolite mixture. 2/6 and 3/6 of the urea/formaldehyde mixture was added dropwise to the other chitosan/zeolite mixtures. All the beakers' mouths were closed to keep the formaldehyde in the mixture and were kept with constant stirring at 70°C for 3 hours. The mixture, which had 3/6 of the urea/formaldehyde, was kept in gel form according to its crosslinking ratio while the others were cast on watch glasses and left to dry. Obtained films and gel were used for adsorption experiments.

3.4 Adsorption Experiments

Reactive Blue 221, Reactive Red 195, Reactive Black 5 and Reactive Yellow 145 were used as adsorbate and each of them were dissolved in distilled water for the experiments. The experiments were done with different pH values, at different temperatures, with different clay-polymer compositions and different cross-linking agent ratios by using chitosan-zeolite non-cross-linked and cross-linked films and cross-linked gel.

3.4.1 Adsorpsion experiments in different pH values

Firstly, the adsorption experiments were done on different pH values. 4 beakers involving 300 ml of distilled water were prepared. Then 15 mg of each dye was added to different beakers and dissolved. Then each dye solution was separated to 3 different jars. So all the 12 jars had 100 ml of dye solutions and we could make sure that each of the solutions with the same color had the same concentration. Then 30 mg of chitosan-zeolite non-crosslinked composites 5:2 (w/w) were added to the dye solutions.

By taking one one jar from each color, 3 groups were prepared to start pH controls. To the first group no NaOH solution was added and they had a pH value around 4. NaOH solution was added and controlled to the other solutions to obtain solutions at the pH value of 6 and 8. As the acid we used diffused in water, it was needed to check the pH often and add some drops of NaOH solution. After the second day the pH values were stable for all the dye solutions. Samples were taken each day the check transmissions by UV-visible spectrophotometry.

3.4.2 Adsorption experiments in different temperatures

4 beakers involving 300 ml of distilled water were prepared. Then 15 mg of each dye was added to different beakers and dissolved. Then each dye solution was separated to 3 different jars. So all the 12 jars had 100 ml of dye solutions and we could make sure that each of the solutions with the same color had the same concentration. Then 30 mg of chitosan-zeolite non-crosslinked composites 5:2 (w/w) were added to the dye solutions.

By taking one one jar from each color, 3 groups were prepared to start the experiments in different temperature values. The experiments were done in different drying ovens at 20°C, 35°C and 50°C. Each solution was controlled to pH value of 6 as it was the best pH value for all of the dyes at the end of the adsorption experiments done before. Samples were taken each day the check transmissions by UV-visible spectrophotometry.

3.4.3 Adsorption experiments in different polymer-clay ratio

4 beakers involving 200 ml of distilled water were prepared. Then 10 mg of each dye was added to different beakers and dissolved. Then each dye solution was separated to 2 different jars. So all the 8 jars had 100 ml of dye solutions and we could make sure that each of the solutions with the same color had the same concentration.

By taking one one jar from each color, 2 groups were prepared to start the experiments in different polymer-clay ratios. Firstly, 30 mg of chitosan-zeolite non-crosslinked composite film 5:2 (w/w) were added to the dye solutions. Then 30 mg of chitosan-zeolite non-crosslinked composite film 5:4 (w/w) were added to the dye solutions. The experiments were examined at the pH value of 6 and 20°C as they had the best results before. Samples were taken each day the check transmissions by UV-visible spectrophotometry.

3.4.4 Adsorption experiments with different cross-linking agent ratio

4 beakers involving 300 ml of distilled water were prepared. Then 15 mg of each dye was added to different beakers and dissolved. Then each dye solution was separated to 3 different jars. So all the 12 jars had 100 ml of dye solutions and we could make sure that each of the solutions with the same color had the same concentration.

By taking one one jar from each color, 3 groups were prepared to start the experiments in different cross-linking agent ratios. To the first group 64.2 mg of chitosan-zeolite film which has low cross-linking ratio was added. To the second group 79.18 mg of chitosan-zeolite film, which has medium cross-linking ratio, was added. To the third group 3 g of chitosan-zeolite gel, which has high cross-linking ratio, was added. All of this adsorbants was calculated to have the same chitosan amount as the non-crosslinked chitosan-zeolite film 5:2 (w/w). The experiments were

examined at the pH value of 6 and 20°C as they had the best results before. Samples were taken each day the check transmissions by UV-visible spectrophotometry.

4. RESULTS AND DISCUSSION

In this study, chitosan/zeolite composites were prepared as decolorant to adsorption textile dyes. Urea and formaldehyde were used in some samples to improve the characteristics of the films prepared.

The films were prepared in 2 different ratio of chitosan/zeolite to have an idea about the effects of the clay used. Urea and formaldehyde were used in 1:2 molar ratio for all the films and gel prepared but they had different amounts of this mixture. The mixtures were air dried on Petri dishes and dried samples were structurally defined by performing FTIR and SEM.

Adsorption experiments were taken with 5 mg of each dye, which were dissolved in 100 ml of distilled water. 30 mg of each composite were added and adsorption performances were examined by checking UV-visible spectrophotometric analyses. The experiments were taken at different pH values and temperatures.

After determination of adsorption capacities, the applicability of adsorption data on the rate equations was investigated and pseudo second order rate equations were fitted to data.

4.1 FTIR Spectrophotometric Analysis

The figure FTIR spectrum of chitosan shows a strong broad peak between 3300 and 3400 cm^{-1} due to –OH group and –NH stretching vibration. The two sharp peaks at 1640 cm-1 and 1540 cm^{-1} due to amide I and II groups. Peak at 1087 cm^{-1} indicates C-O stretching and 1485 cm^{-1} due to C-N stretching. And the peak at 1320 cm^{-1} is specific for chitosan. There is an increase of N-H stretching (Figure 4.3) according to urea-formaldehyse resin. Also, due to C-N stretching, a peak at 1257 cm^{-1} observed. From the FTIR spectra (Figure 4.2) a clear peak at 1560-1570 cm^{-1} is obtained due to NH_3^+group shows interaction between chitosan and zeolite.

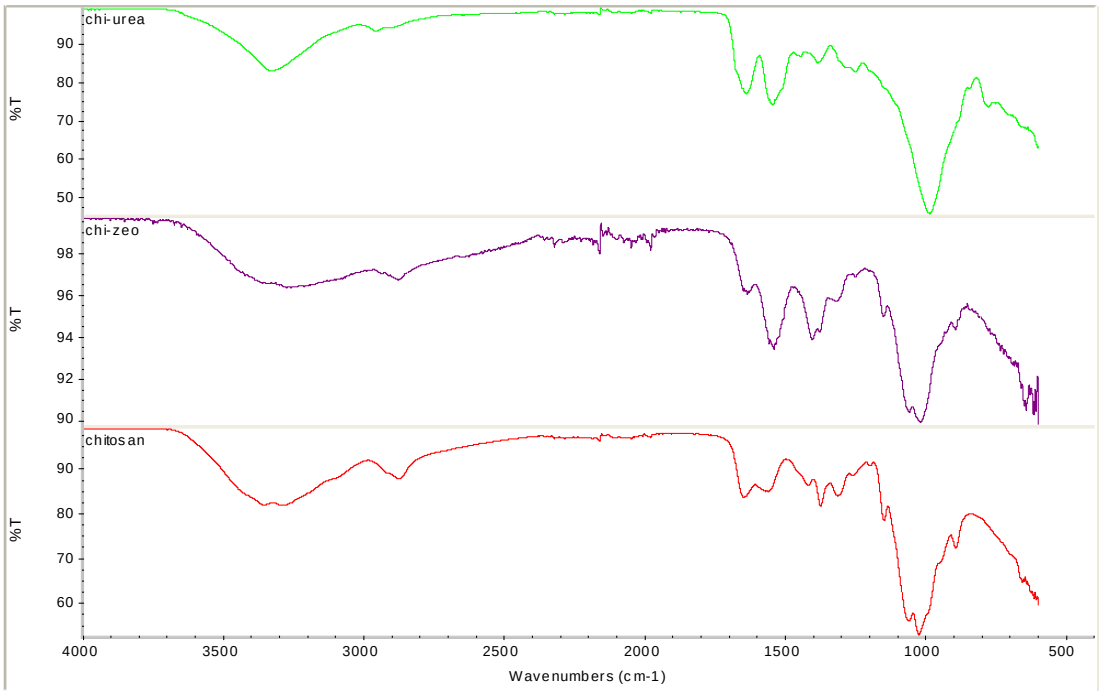


Figure 4.1 : FTIR comparison of the chitosan(red), chitosan/zeolite(purple) and chitosan/zeolite crosslinked by UF (green)

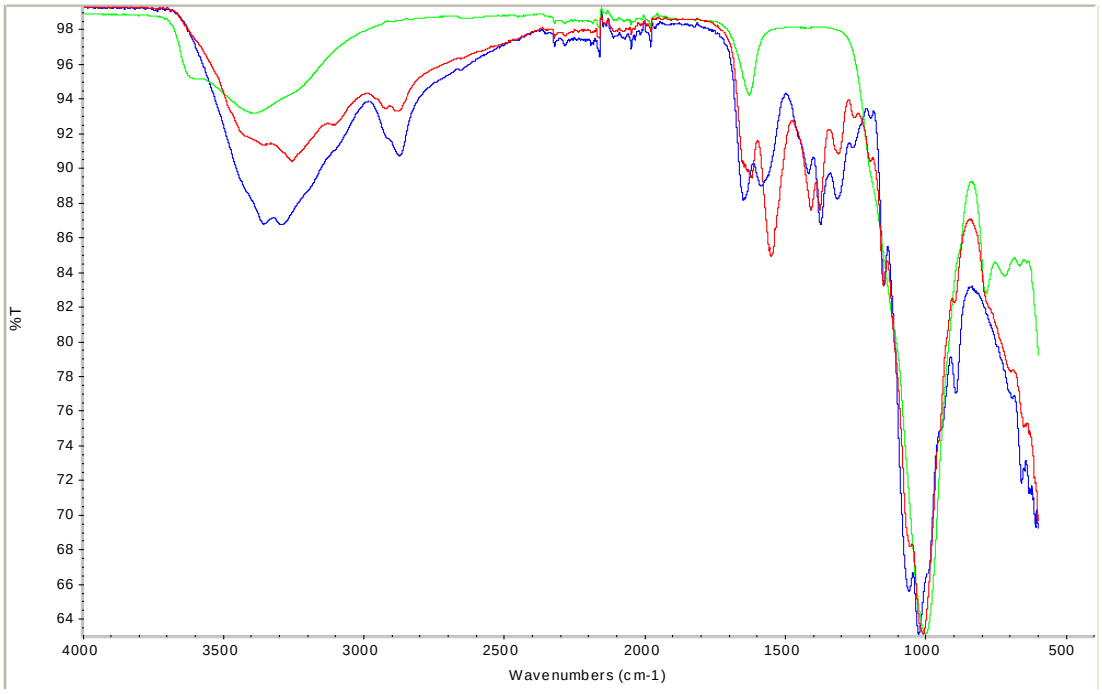


Figure 4.2 : FTIR comparison of chitosan(blue), zeolite(green), chitosan-zeolite composite(red)

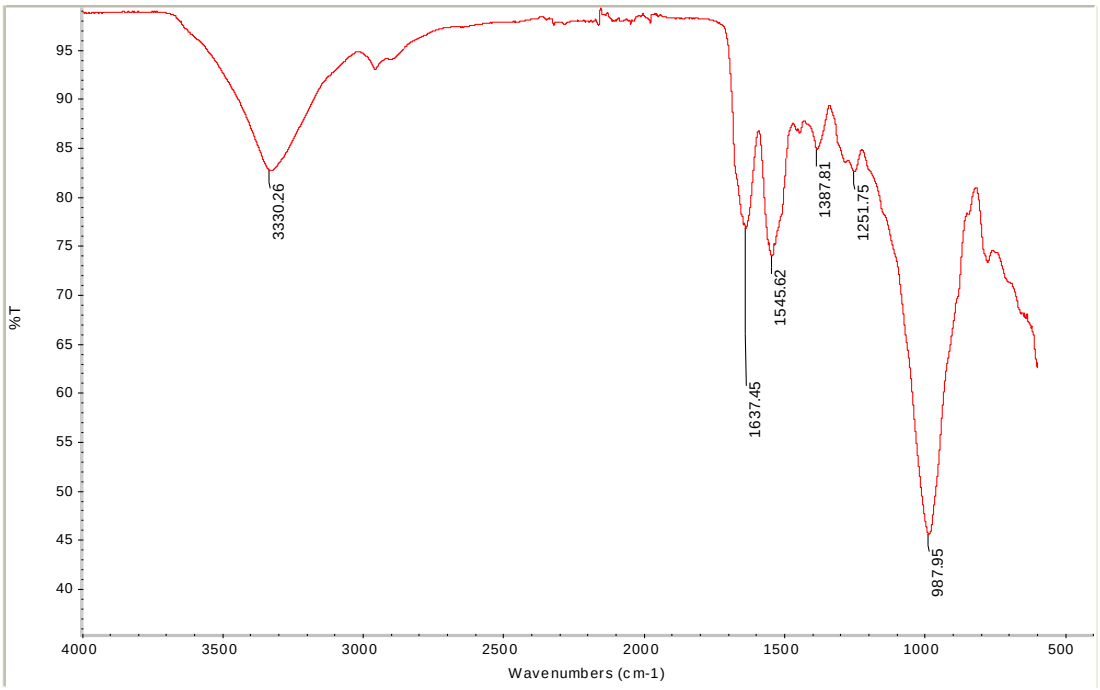


Figure 4.3 : FTIR of UF cross-linked chitosan/zeolite composite

4.2 Scanning Electron Microscopy (SEM)

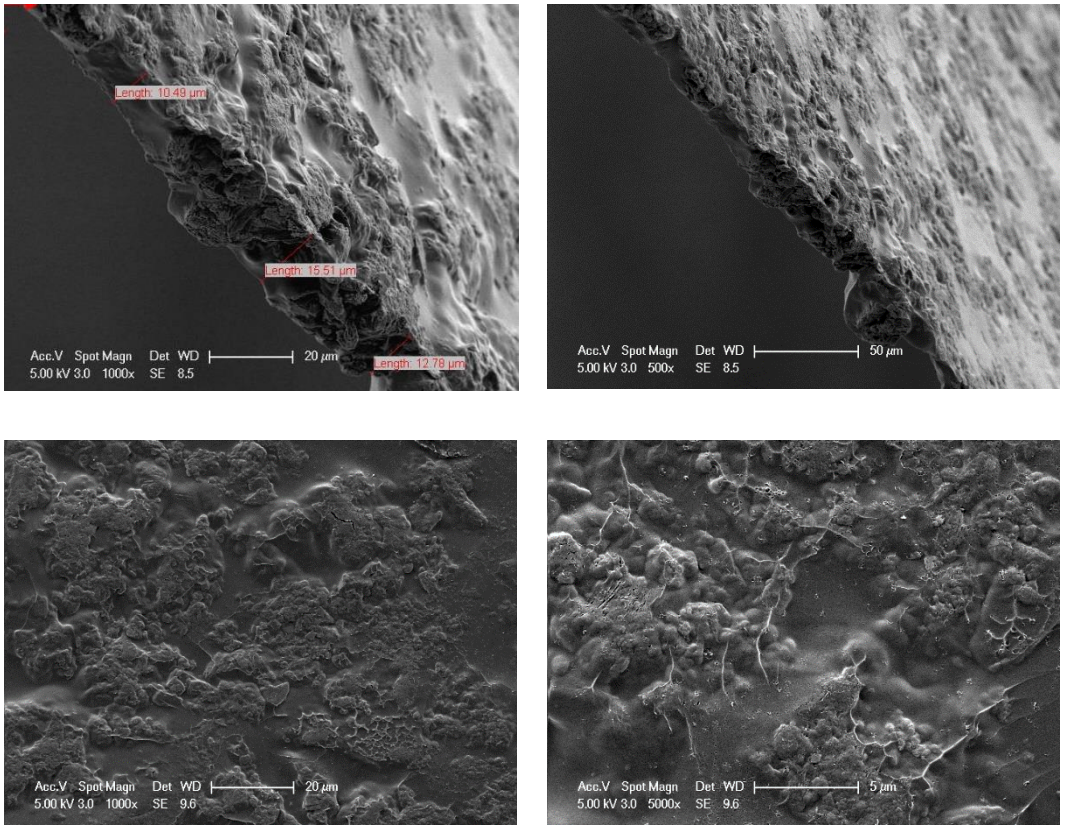


Figure 4.4 : SEM of non-crosslinked chitosan/zeolite composite film

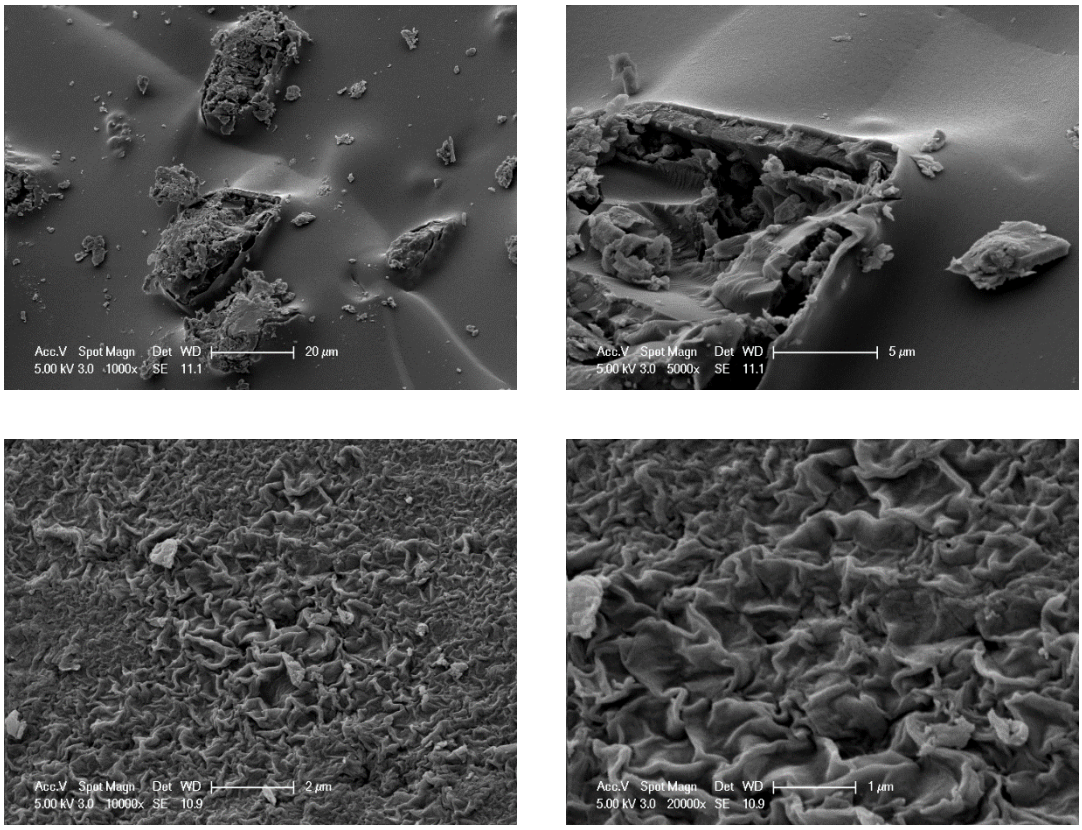


Figure 4.5 : SEM of UF crosslinked chitosan/zeolite composite(dried from gel form)

SEM analyses' results show that the thickness of the composite films obtained is 10 to 20 µm (Figure 4.4). The thickness mostly depended on the size of zeolite clay used. Composite surface is quite smooth but the surface area depended on zeolite clay, which increased the area. Clay also caused macropores (when the pore size is greater than 50 nm) to the film. SEM images of UF crosslinked chitosan/zeolite composite (Figure 4.5) show that the composite have a rough and irregular surface morphology. As the sample obtained from the gel form, the analyses does not directly give an idea about the phase used in process. Some areas on the surface show high surface area while some parts have smooth surfaces and pores.

4.3 Adsorption Capacities

4.3.1 The effect of pH

The adsorption experiments were done by using chitosan/zeolite 5:2 composite films to decide the best pH value for the further experiments. The best results in long time

adsorption were generally taken at pH 6 and the adsorption rate was controlled while the best results in short time adsorption were taken at pH 4.

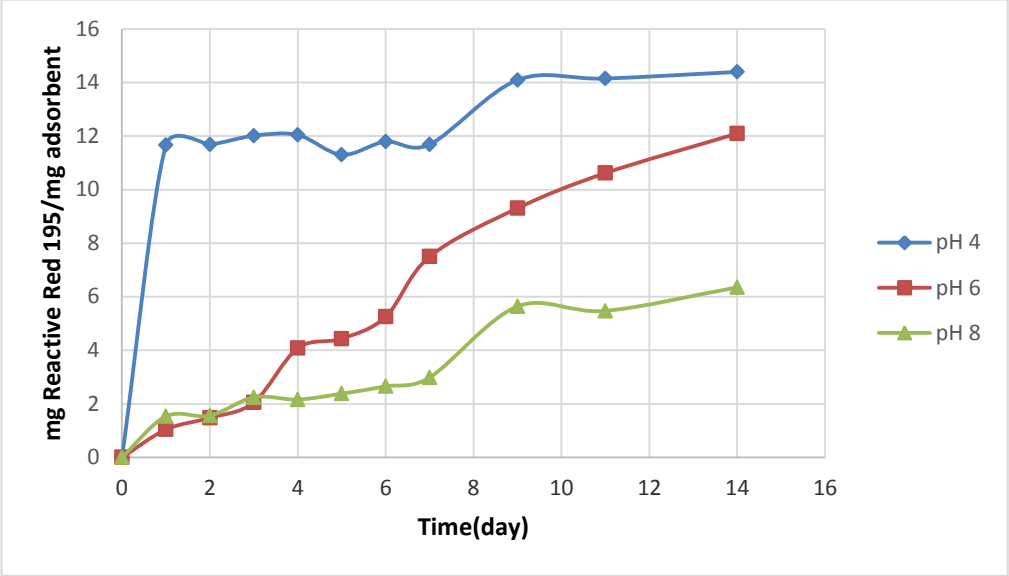


Figure 4.6 : The change of adsorption capacity versus time for different pH values RR195 (Dye concentration= 50mg/L, 30 mg composite, T=20°C)

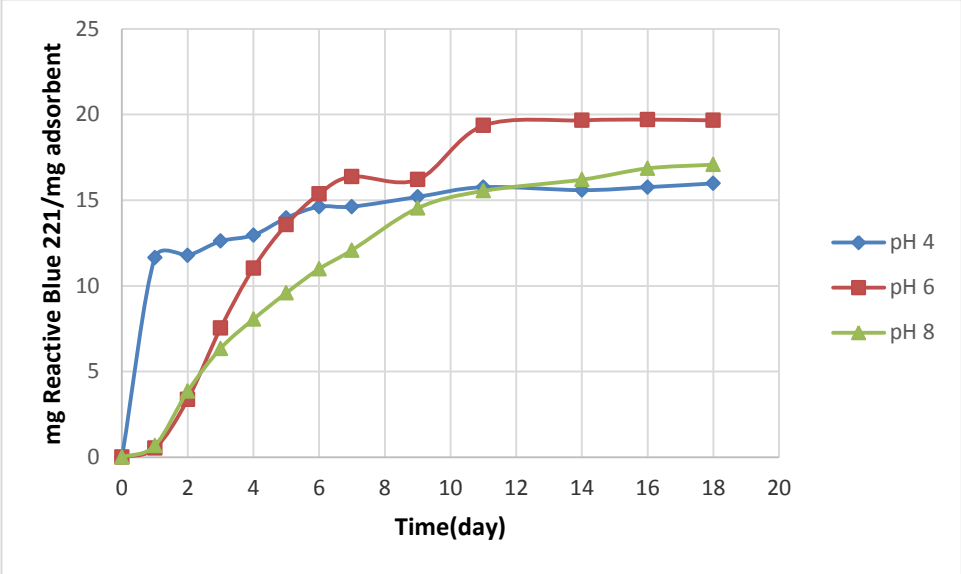


Figure 4.7 : The change of adsorption capacity versus time for different pH values RB221 (Dye concentration= 50mg/L, 30 mg composite, T=20°C)

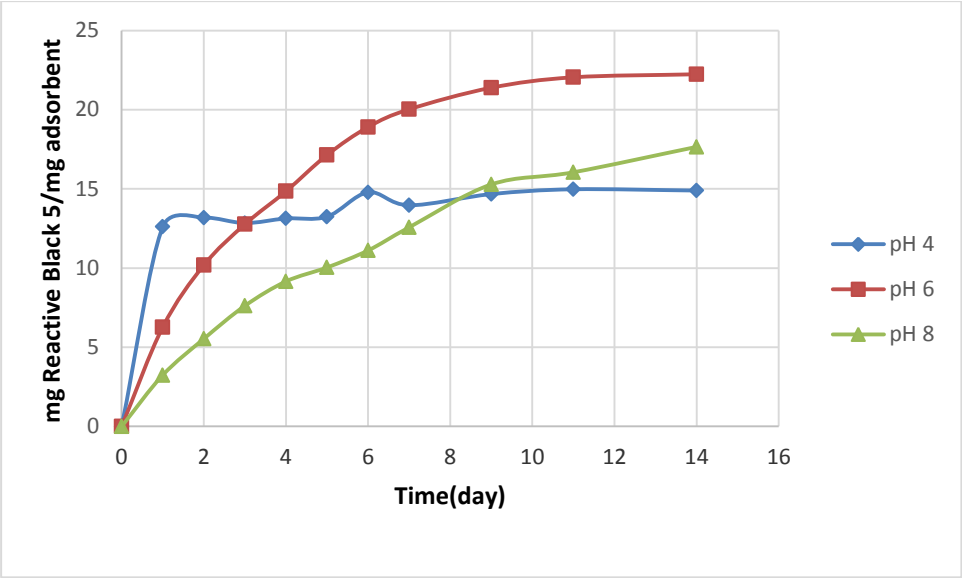


Figure 4.8 : The change of adsorption capacity versus time for different pH values RB5 (Dye concentration= 50mg/L, 30 mg composite, T=20°C)

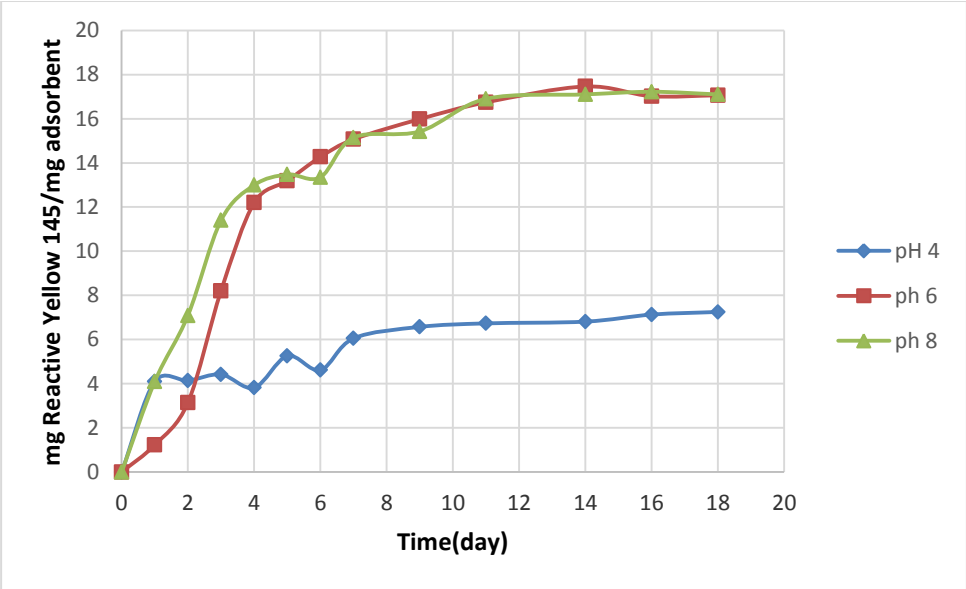


Figure 4.9 : The change of adsorption capacity versus time for different pH values RY145 (Dye concentration= 50mg/L, 30 mg composite, T=20°C)

The adsorption capacities of Reactive Red 195 were found 14.39, 12.10 and 6.35(mg dye/mg adsorbent) at pH 4, pH 6 and pH 8. The adsorption capacities of Reactive Blue 221 were found 15.89, 19.66 and 17.07(mg dye/mg adsorbent) at pH 4, pH 6 and pH 8. The adsorption capacities of Reactive Black 5 were found as 14.89, 22.24 and 17.65(mg dye/mg adsorbent) adsorbent at pH 4, pH 6 and pH 8. The adsorption capacities of Reactive Yellow 145 were found as 7.25, 17.21 and 17.10(mg dye/mg adsorbent) at pH 4, pH 6 and pH 8. Optimum pH was found as pH 6 for long time adsorption through the adsorption capacities.

4.3.2 The effect of temperature

Adsorption experiments were done at 20°C, 35°C and 50°C. In short time there was not much difference between the adsorption capacities. The best results were obtained shown at low temperature (20°C) and it shows that adsorption experiment of textile dyes by chitosan/zeolite composites is exothermic.

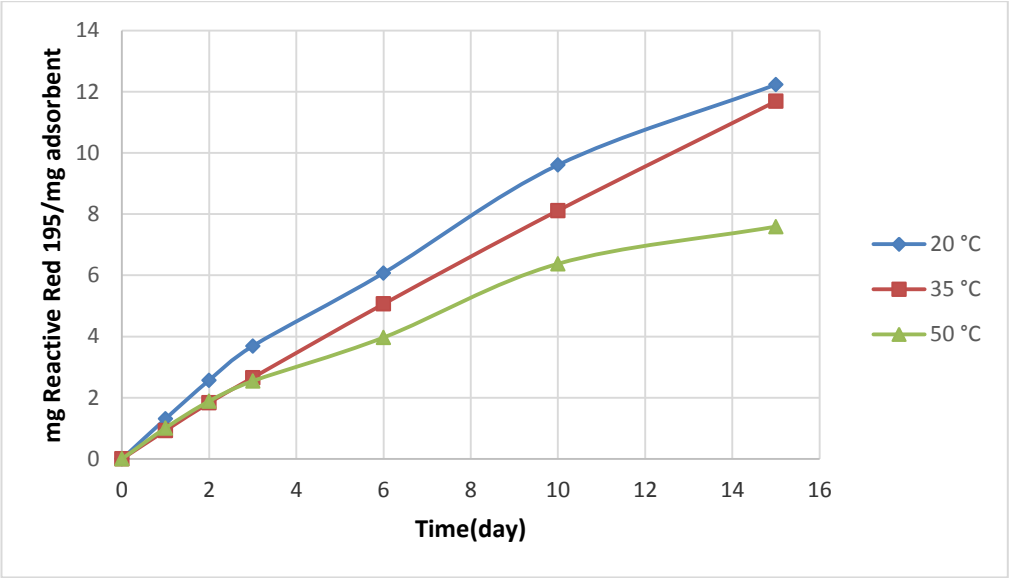


Figure 4.10 : The change of adsorption capacity versus time for different T values RR195 (Dye concentration= 50mg/L, 30 mg composite, pH 6)

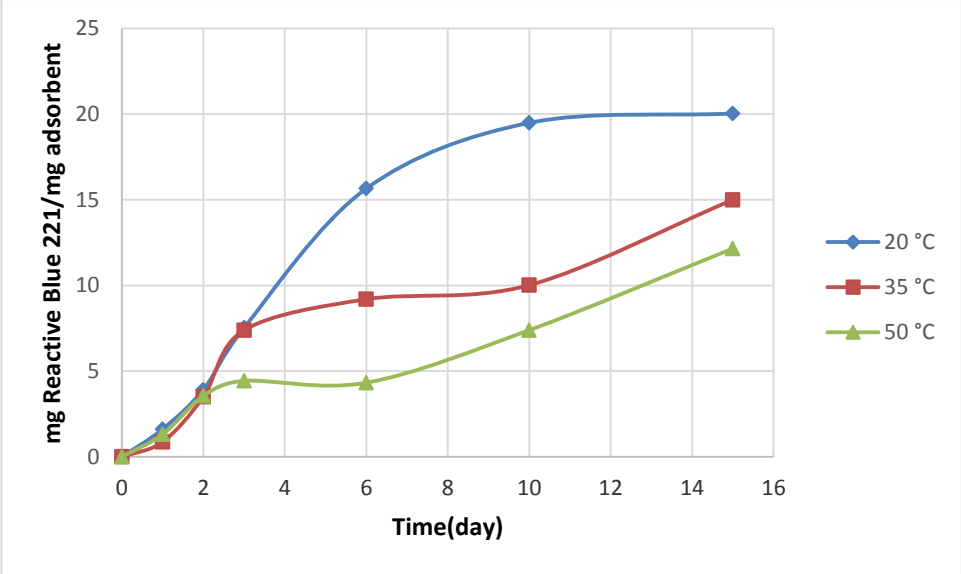


Figure 4.11 : The change of adsorption capacity versus time for different T values RB221 (Dye concentration= 50mg/L, 30 mg composite, pH 6)

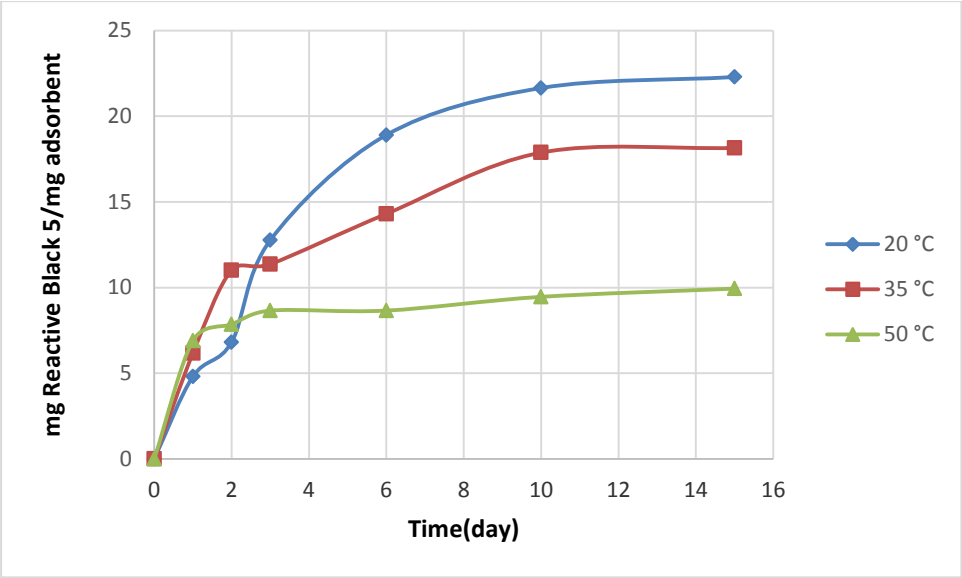


Figure 4.12 : The change of adsorption capacity versus time for different T values RB5 (Dye concentration= 50mg/L, 30 mg composite, pH 6)

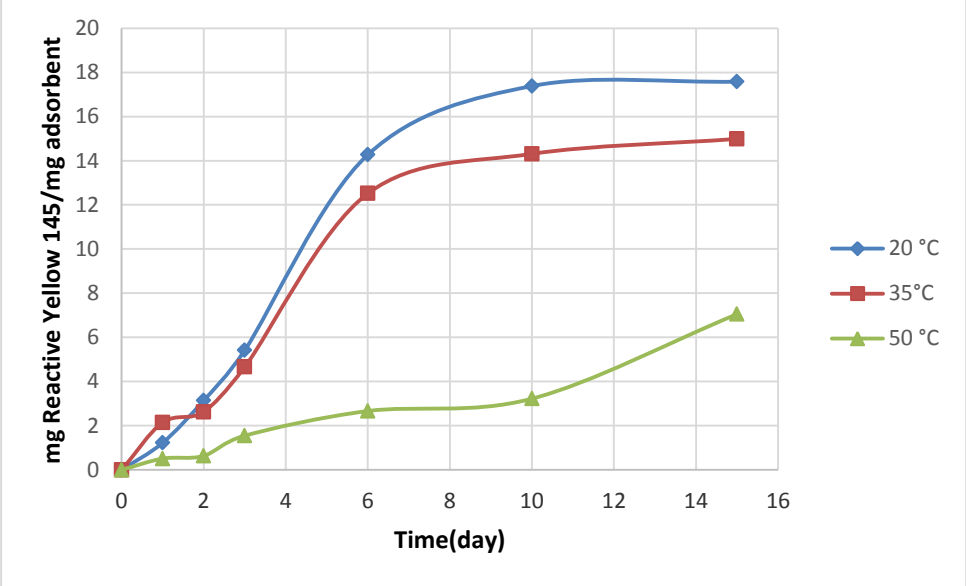


Figure 4.13 : The change of adsorption capacity versus time for different T values RT145 (Dye concentration= 50mg/L, 30 mg composite, pH 6)

The adsorption capacities of Reactive Red 195 were found 12.23, 11.68 and 10.97(mg dye/mg adsorbent) at 20°C, 35°C and 50°C. The adsorption capacities of Reactive Blue 221 were found 20.03, 15 and 12.15(mg dye/mg adsorbent) at 20°C, 35°C and 50°C. The adsorption capacities of Reactive Black 5 were found as 22.30, 18.15, 9.95(mg dye/mg adsorbent) adsorbent at 20°C, 35°C and 50°C. The adsorption capacities of Reactive Yellow 145 were found as 17.58, 14 and 7.05(mg

dye/mg adsorbent) at 20°C, 35°C and 50°C. Optimum temperature was found as 20°C for long time adsorption.

4.3.3 The effect clay ratio

The adsorption experiments were done by using zeolite/chitosan 0.4:1 and 0.8:1 composite films to have an idea about the effect of clay ratio. The experiments resulted as shown in the graphs below.

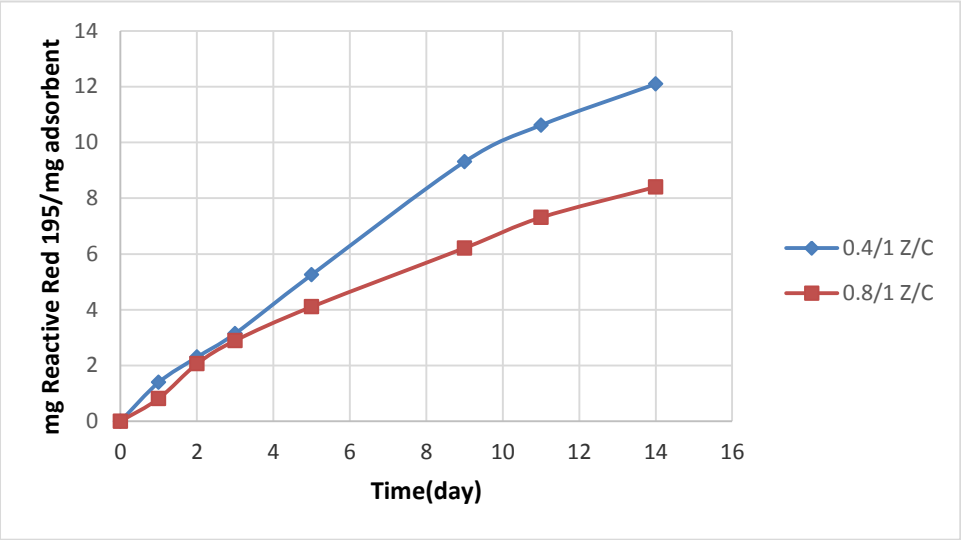


Figure 4.14 : The change of adsorption capacity versus time for different clay ratio RR195 (Dye concentration= 50mg/L, 30 mg composite, pH 6, T=20°C)

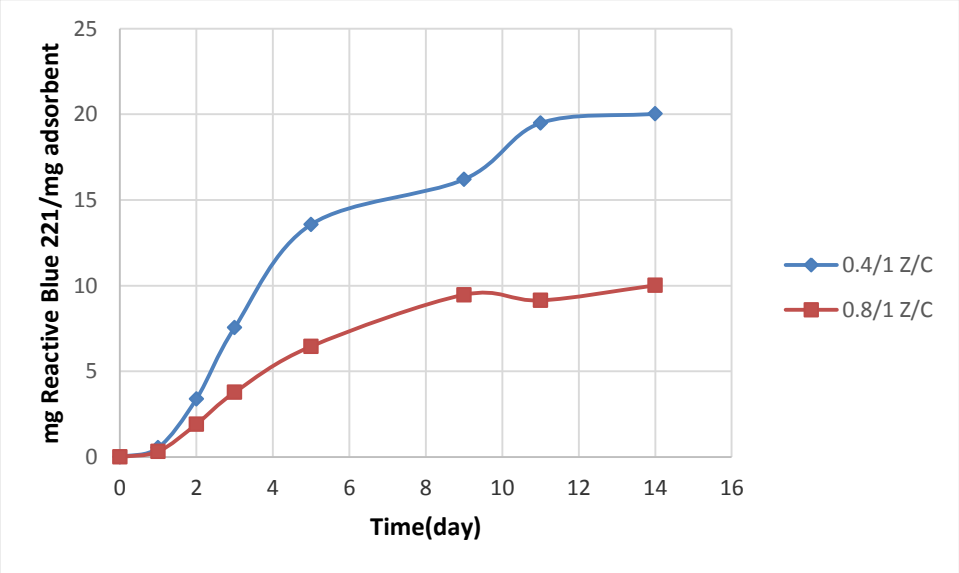


Figure 4.15 : The change of adsorption capacity versus time for different clay ratio RB221 (Dye concentration= 50mg/L, 30 mg composite, pH 6, T=20°C)

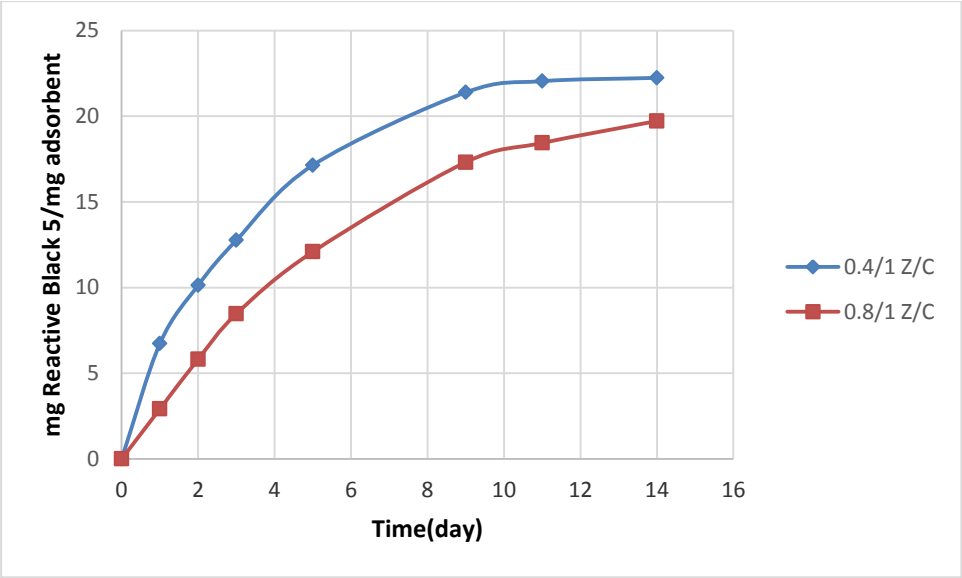


Figure 4.16 : The change of adsorption capacity versus time for different clay ratio RB5 (Dye concentration= 50mg/L, 30 mg composite, pH 6, T=20°C)

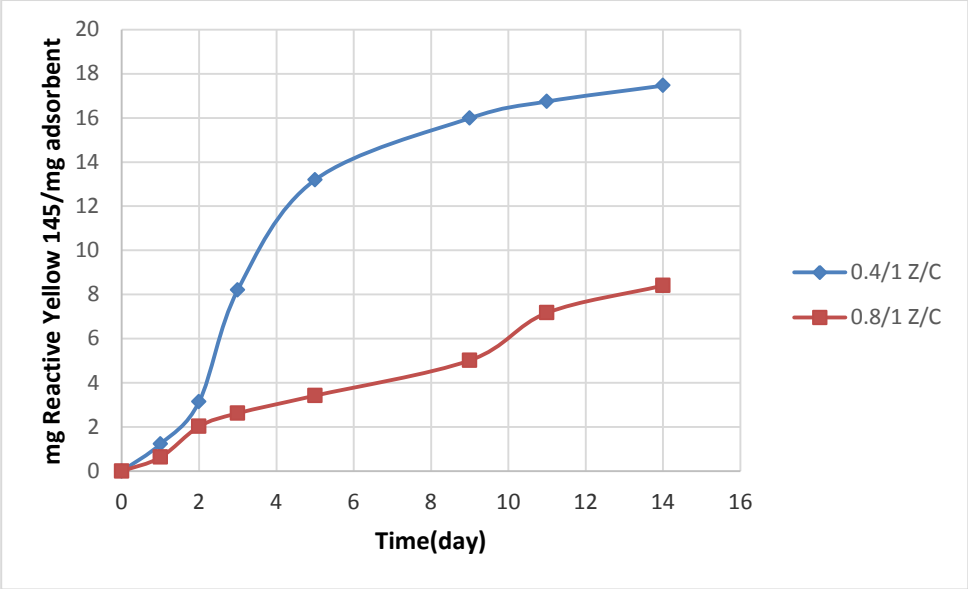


Figure 4.17 : The change of adsorption capacity versus time for different clay ratio RY145 (Dye concentration= 50mg/L, 30 mg composite, pH 6, T=20°C)

The adsorption capacities of Reactive Red 195 were found 12.10 and 8.80(mg dye/mg adsorbent) for 0.4:1 and 0.8:1 clay ratio. The adsorption capacities of Reactive Blue 221 were found 20.03 and 10.01(mg dye/mg adsorbent) for 0.4:1 and 0.8:1 clay ratio. The adsorption capacities of Reactive Black 5 were found as 22.24 and 19.72(mg dye/mg adsorbent) adsorbent for 0.4:1 and 0.8:1 clay ratio. The adsorption capacities of Reactive Yellow 145 were found as 17.46 and 8.40(mg

dye/mg adsorbent) for 0.4:1 and 0.8:1 clay ratio. 0.4:1 ratio gives better results for all the experiments. Although for Reactive Black 5 it must be optimized for industry.

4.3.4 The effect of cross-linking agent

Adsorption experiments were repeated with different urea-formaldehyde (UF) ratios. In short time there was not much difference between the adsorption capacities. The best results were obtained with high UF ratio.

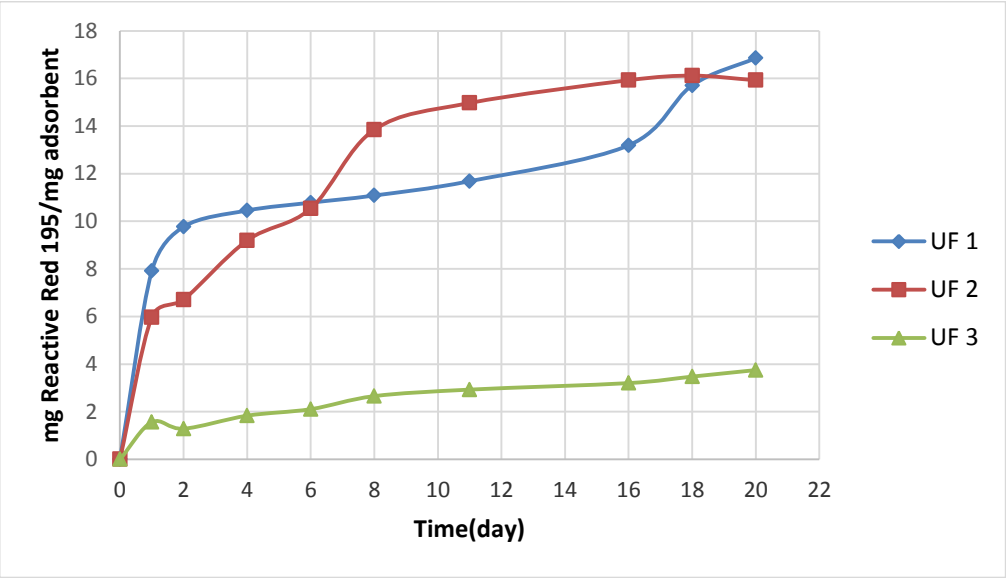


Figure 4.18 : The change of adsorption capacity versus time for different cross-linking ratio. RR195 (Dye concentration= 50mg/L, pH 6, T=20°C)

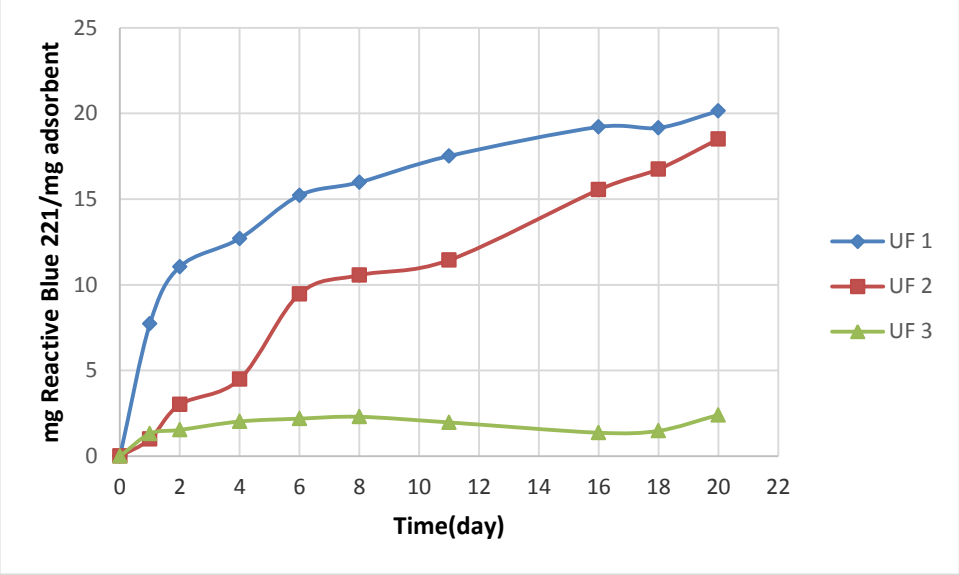


Figure 4.19 : The change of adsorption capacity versus time for different cross-linking ratio. RB221 (Dye concentration= 50mg/L, pH 6, T=20°C)

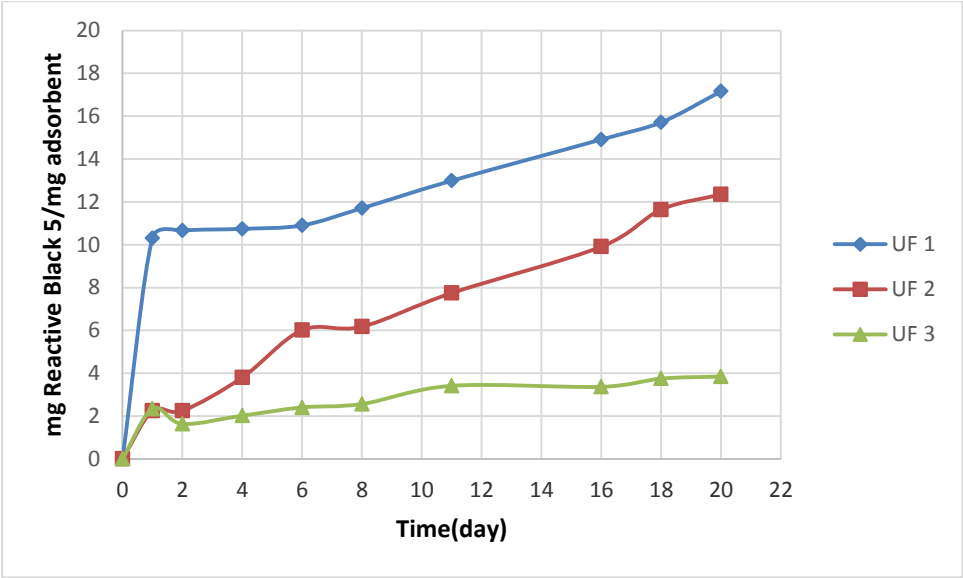


Figure 4.20 : The change of adsorption capacity versus time for different cross-linking ratio. RB5 (Dye concentration= 50mg/L, pH 6, T=20°C)

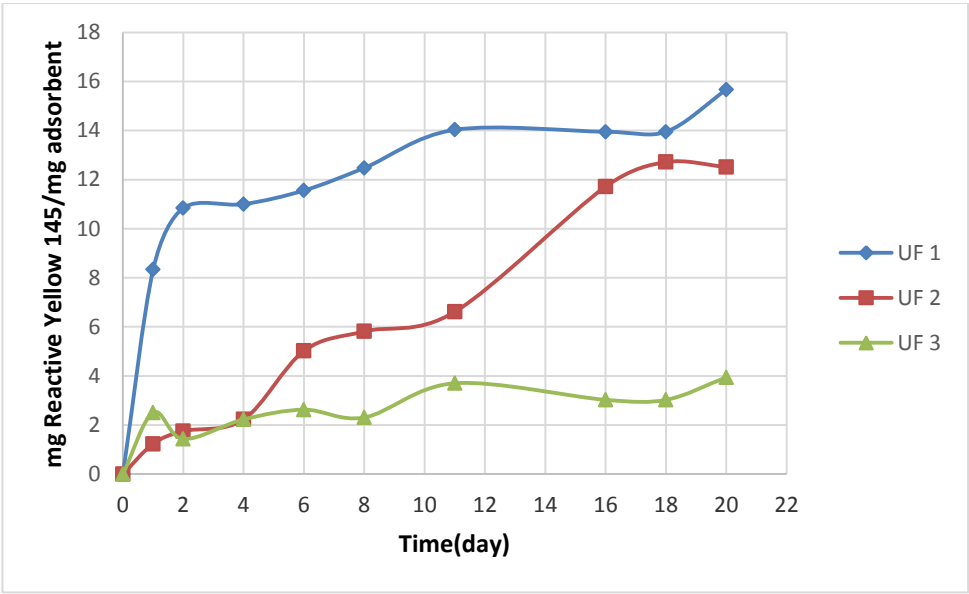


Figure 4.21 : The change of adsorption capacity versus time for different cross-linking ratio. RY145 (Dye concentration= 50mg/L, pH 6, T=20°C)

The adsorption capacities of Reactive Red 195 were found 16.86, 15.93 and 3.75(mg dye/mg adsorbent) at high, medium and low UF ratio. The adsorption capacities of Reactive Blue 221 were found 20.14, 18.50 and 2.40(mg dye/mg adsorbent) at high, medium and low UF ratio. The adsorption capacities of Reactive Black 5 were found as 17.15, 13.34 and 3.85(mg dye/mg adsorbent) adsorbent at high, medium and low UF ratio. The adsorption capacities of Reactive Yellow 145 were found as 15.66, 12.51 and 3.94(mg dye/mg adsorbent) at high, medium and low UF ratio. The results show that high UF ratio has good effect for both short and long-term adsorption.

4.3.5 Optimum conditions for short term adsorption

All of the samples gave the best results at pH 4 for the first day while the best adsorption capacities were obtained at pH 6 for long term. As the best results were obtained with non-crosslinked composite and highly crosslinked one, the experiments were repeated with optimum conditions of short-term adsoption with high adsorbent amount.

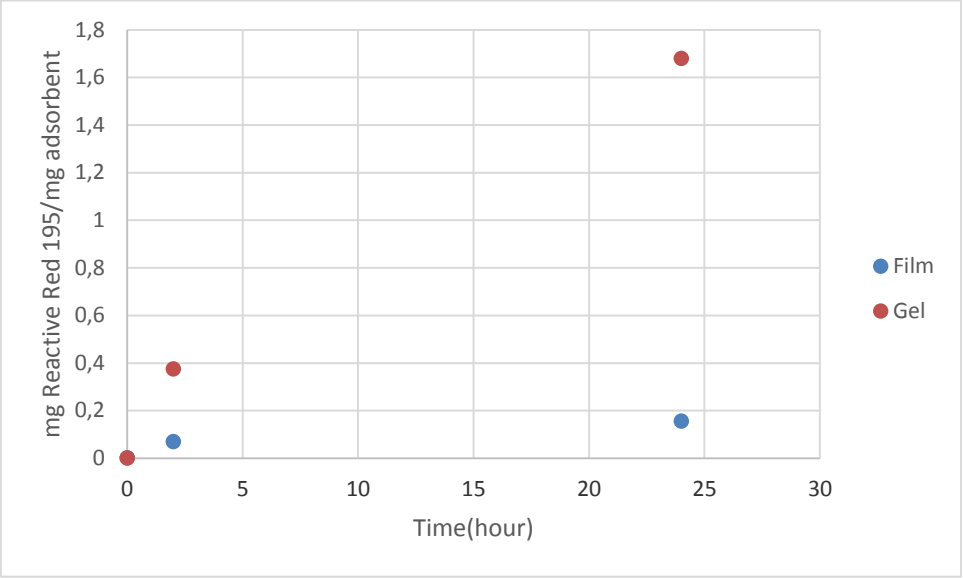


Figure 4.22 : The change of adsorption capacity versus time in optimum conditions. RR195 (Dye concentration= 25mg/L, pH 4, T=20°C)

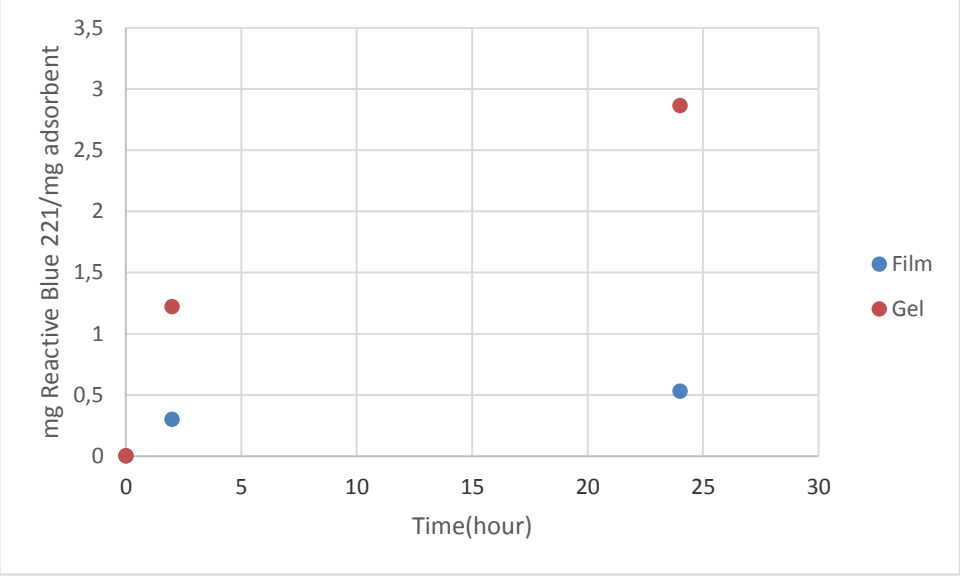


Figure 4.23 : The change of adsorption capacity versus time in optimum conditions. RB221 (Dye concentration= 25mg/L, pH 4, T=20°C)

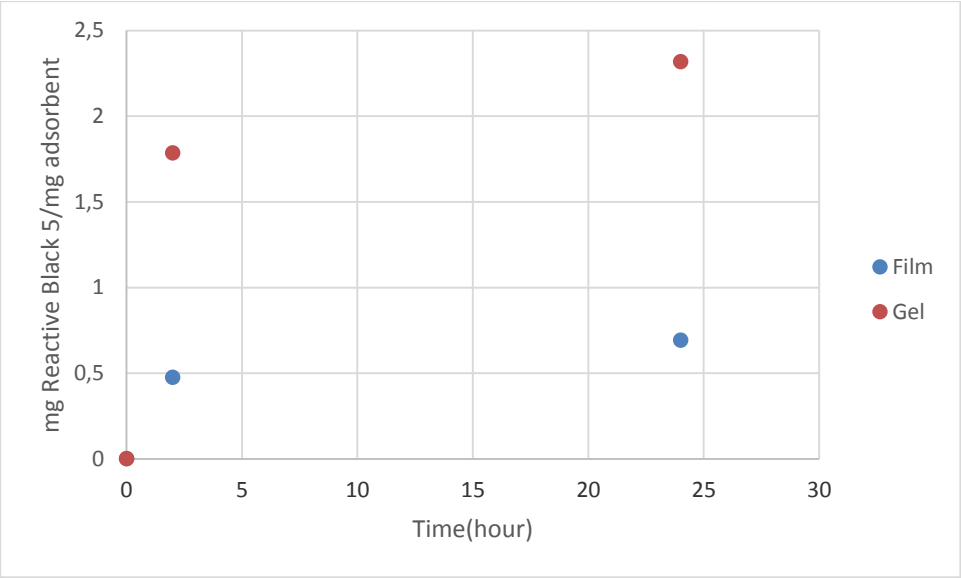


Figure 4.24 : The change of adsorption capacity versus time in optimum conditions. RB5 (Dye concentration= 25mg/L, pH 4, T=20°C)

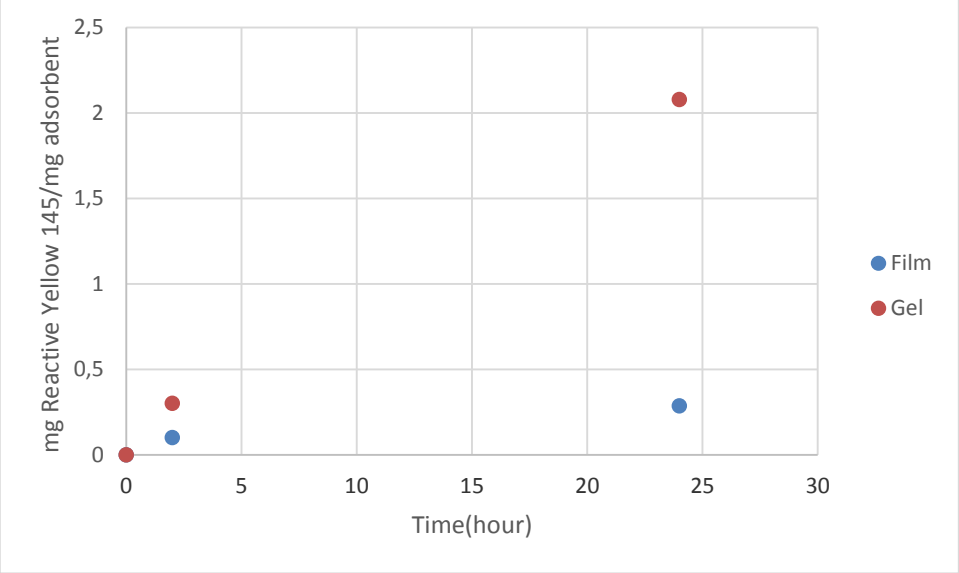


Figure 4.25 : The change of adsorption capacity versus time in optimum conditions. RY145 (Dye concentration= 25mg/L, pH 4, T=20°C)

The adsorption capacities of Reactive Red 195 were found 0.07 and 0.37(mg dye/mg adsorbent) at the end of 2 h and 0.16 and 1.68(mg dye/mg adsorbent) at the endfor composite film (0.4:1) and gel (UF 1). For Reactive Blue 221 were found 0.30 and 1.22(mg dye/mg adsorbent) at the end of 2 h and 0.53 and 2.86(mg dye/mg adsorbent) at the end. For Reactive Black 5 were found as 0.48 and 1.79(mg dye/mg adsorbent) at the end of 2 h and 0.69 and 2.32(mg dye/mg adsorbent) at the end. For Reactive Yellow 145 were found as 0.10 and 0.30(mg dye/mg adsorbent) at the end of 2 h and 0.29 and 2.08(mg dye/mg adsorbent) at the end.

4.4 Adsorption Kinetics Studies

Kinetic studies were examined with both pseudo-first order rate equation and pseudo second order rate equation. Pseudo-second order rate equation was found as the suitable one and its plots were presented below.

4.4.1 Application of pseudo second order rate equation for different pH values

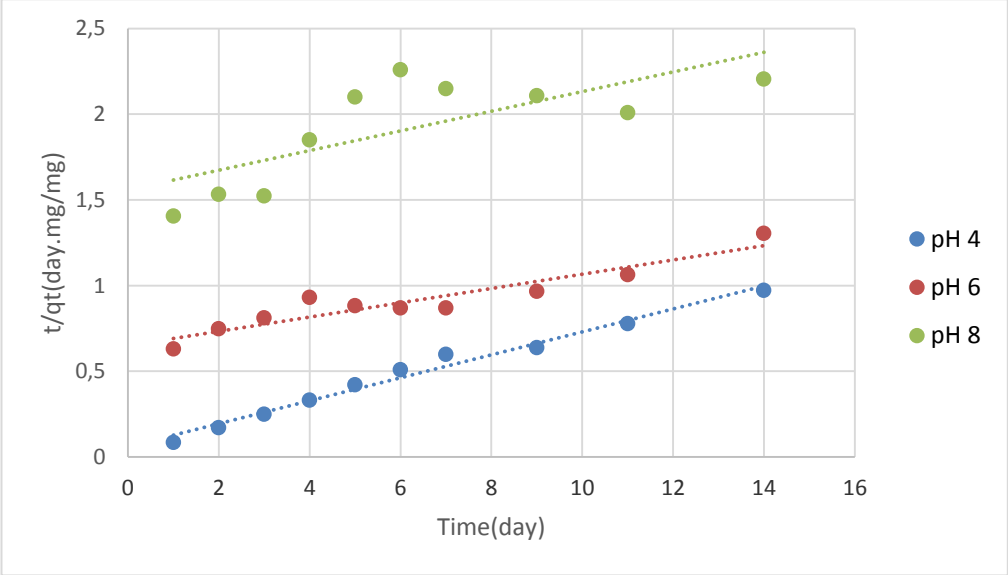


Figure 4.26 : Application of pseudo second order rate equation for different pH values RR195 (Dye concentration= 50mg/L, 30 mg composite, T=20°C)

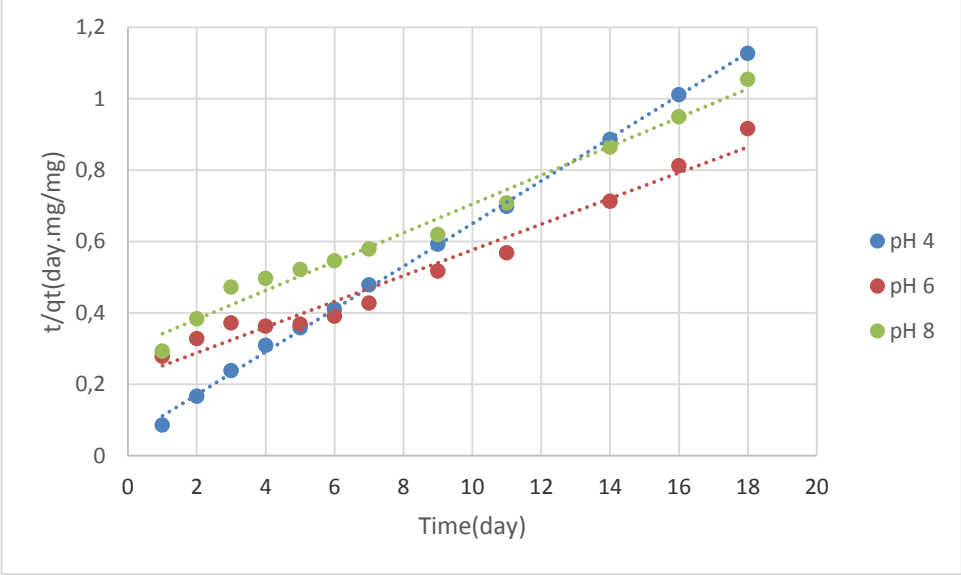


Figure 4.27 : Application of pseudo second order rate equation for different pH values RB221 (Dye concentration= 50mg/L, 30 mg composite, T=20°C)

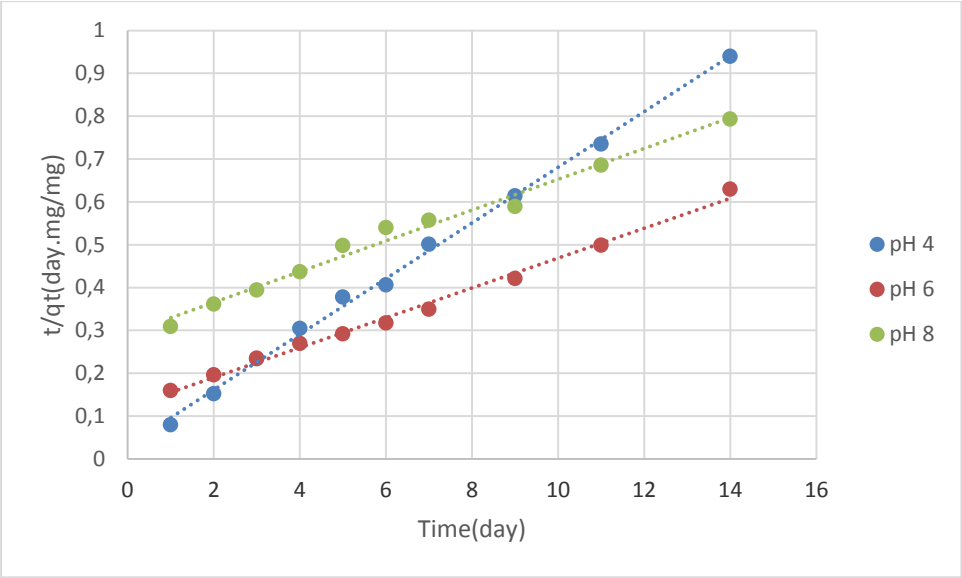


Figure 4.28 : Application of pseudo second order rate equation for different pH values RB5 (Dye concentration= 50mg/L, 30 mg composite, T=20°C)

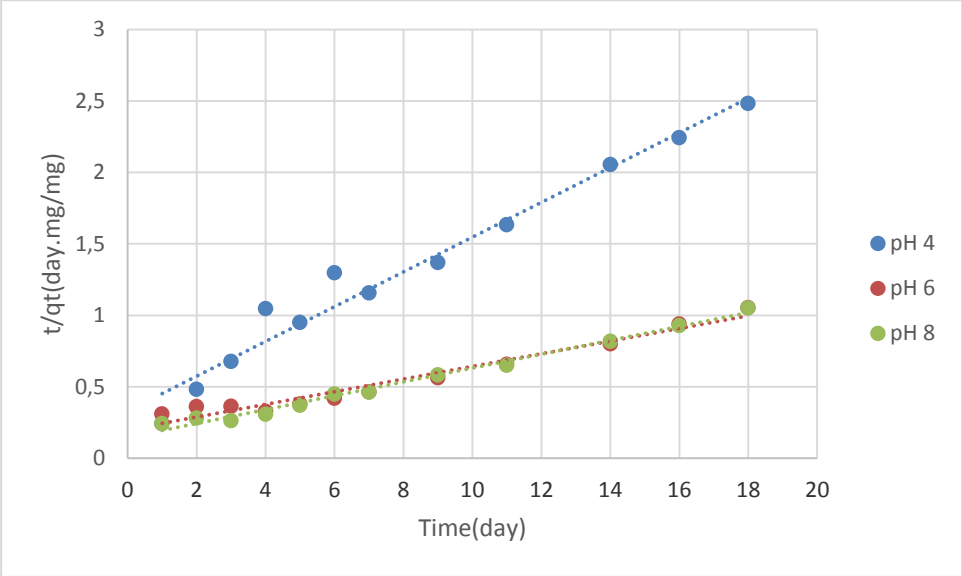


Figure 4.29 : Application of pseudo second order rate equation time for different pH values RY145 (Dye concentration= 50mg/L, 30 mg composite, T=20°C)

4.4.2 Application of pseudo second order rate equation for different temperatures

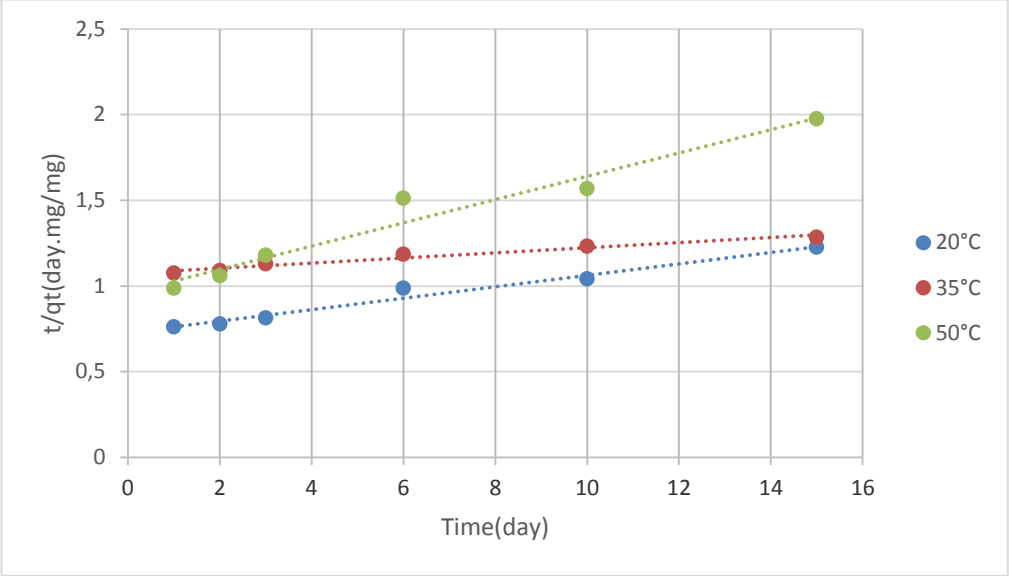


Figure 4.30 : Application of pseudo second order rate equation for different T values RR195 (Dye concentration= 50mg/L, 30 mg composite, pH 6)

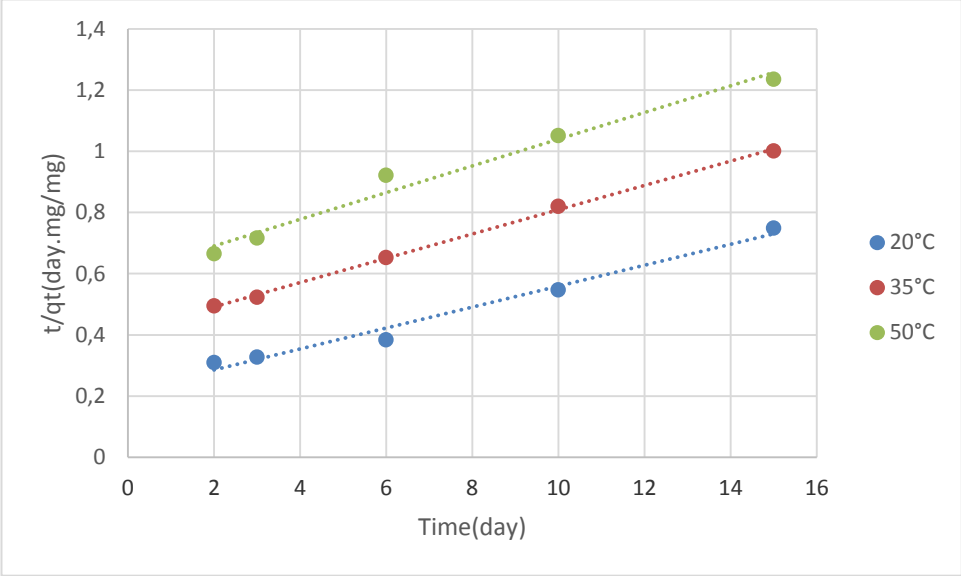


Figure 4.31 : Application of pseudo second order rate equation for different T values RB221 (Dye concentration= 50mg/L, 30 mg composite, pH 6)

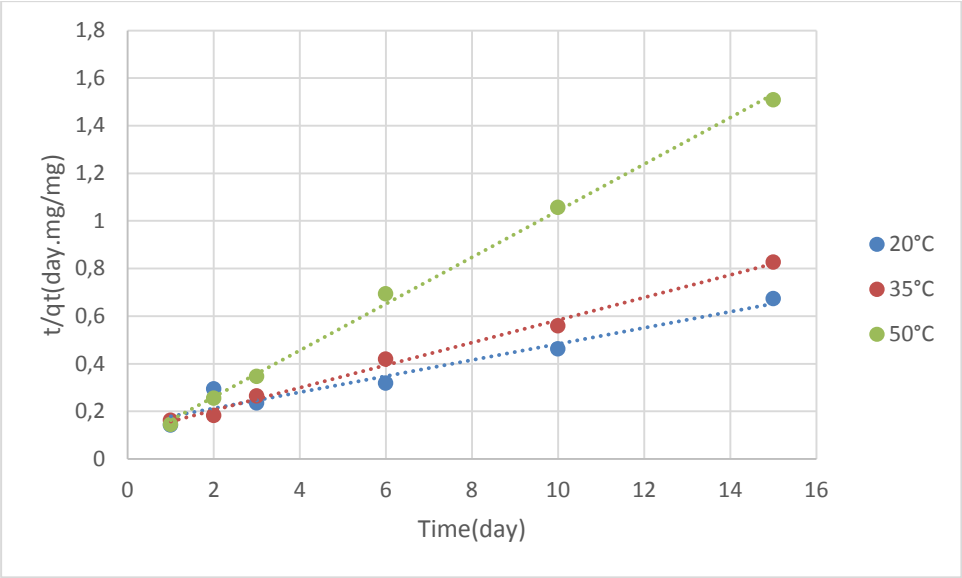


Figure 4.32 : Application of pseudo second order rate equation for different T values RB5 (Dye concentration= 50mg/L, 30 mg composite, pH 6)

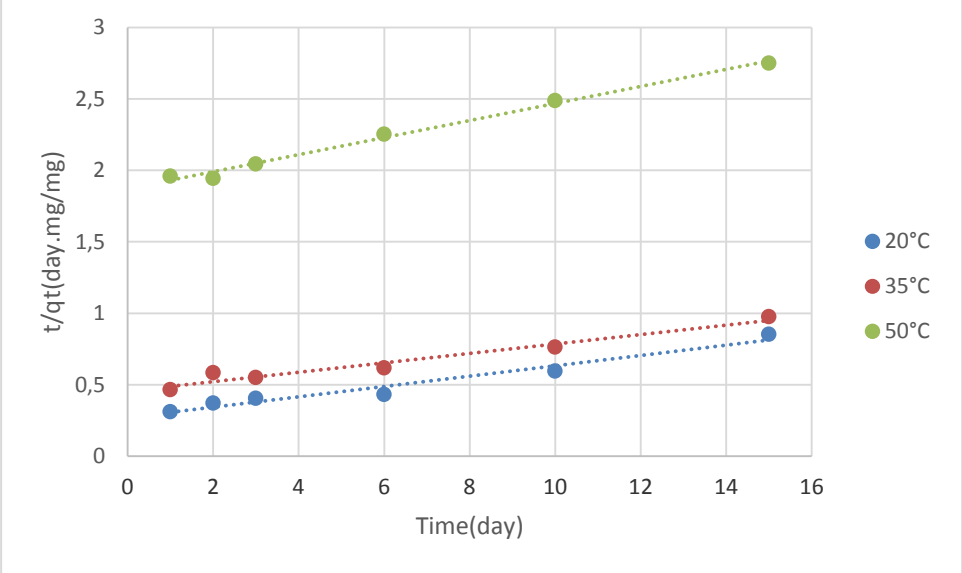


Figure 4.33 : Application of pseudo second order rate equation for different T values RY145 (Dye concentration= 50mg/L, 30 mg composite, pH 6)

4.4.3 Application of pseudo second order rate equation for different ratios of clay

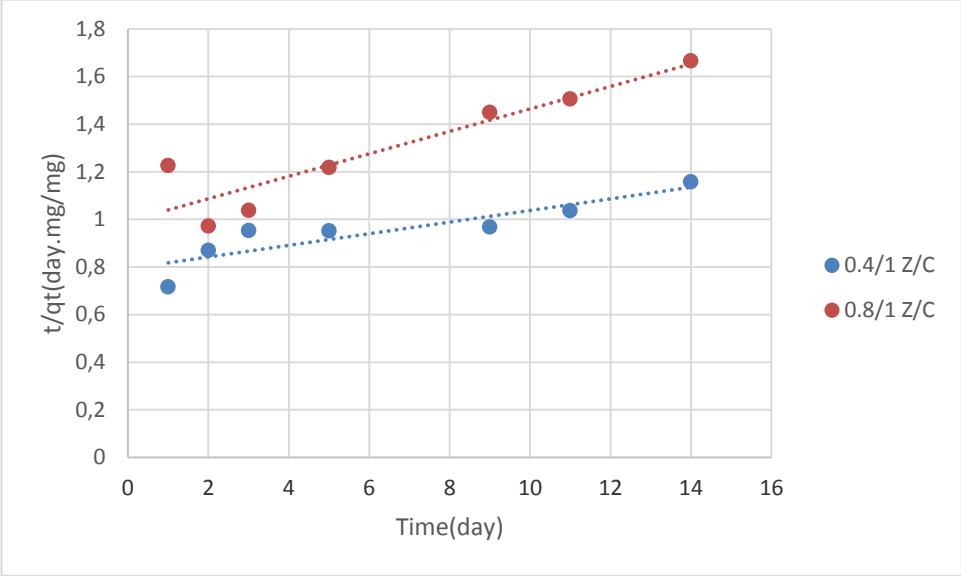


Figure 4.34 : Application of pseudo second order rate equation for different clay ratio RR195 (Dye concentration= 50mg/L, 30 mg composite, pH 6, T=20°C)

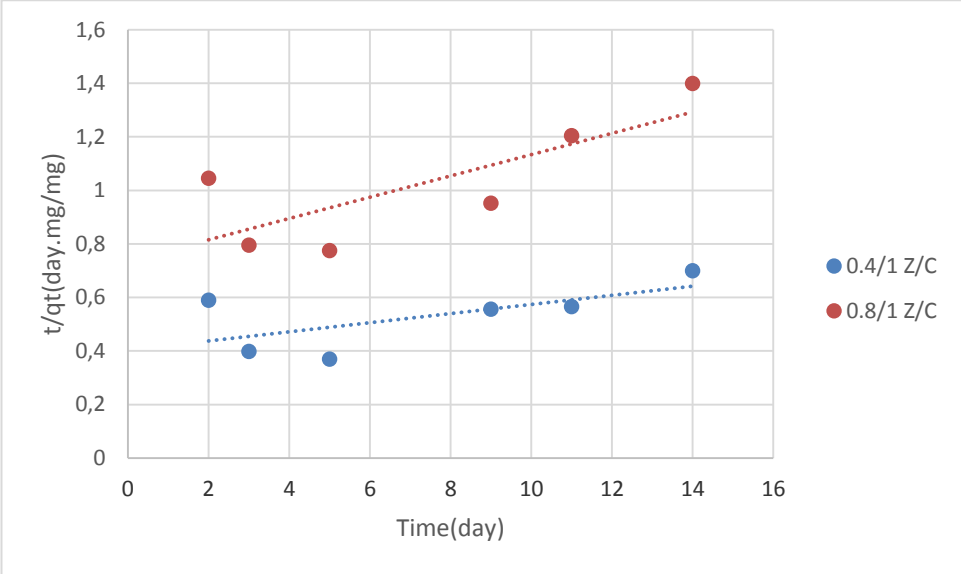


Figure 4.35 : Application of pseudo second order rate equation time for different clay ratio RB221 (Dye concentration= 50mg/L, 30 mg composite, pH 6, T=20°C)

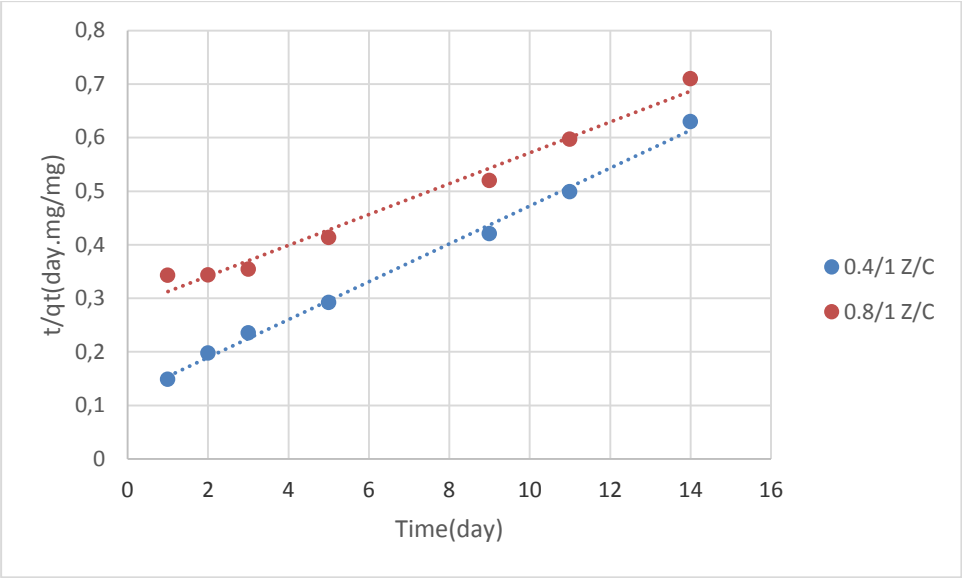


Figure 4.36 : Application of pseudo second order rate equation for different clay ratio RB5 (Dye concentration= 50mg/L, 30 mg composite, pH 6, T=20°C)

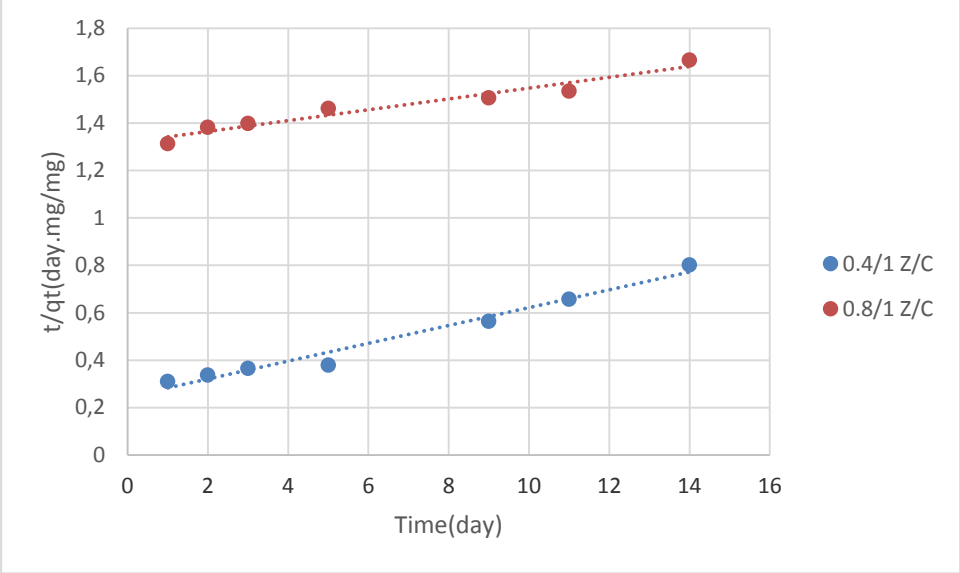


Figure 4.37 : Application of pseudo second order rate equation for different clay ratio RY145 (Dye concentration= 50mg/L, 30 mg composite, pH 6, T=20°C)

4.4.4 Application of pseudo second order rate equation for different amount of cross-linking agent

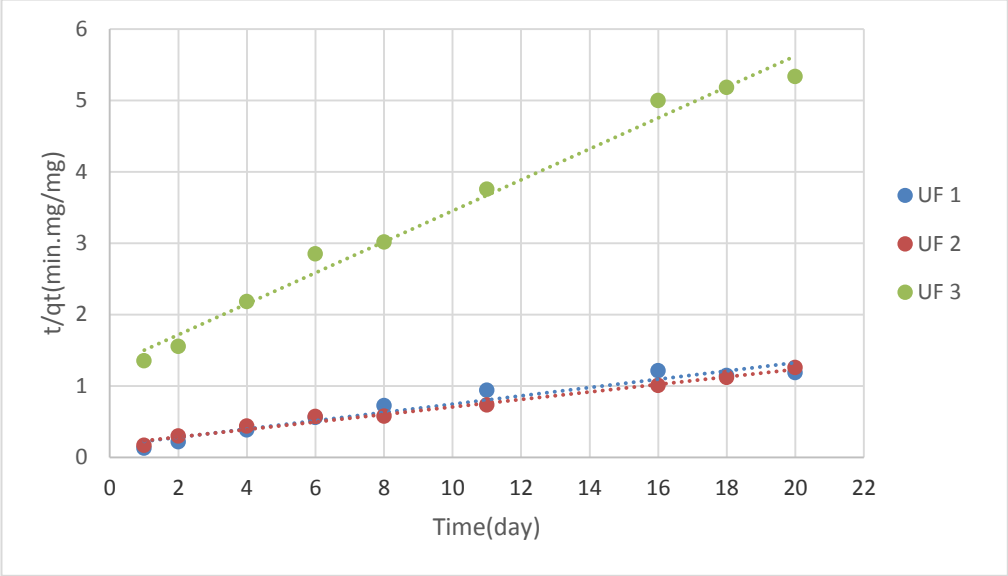


Figure 4.38 : Application of pseudo second order rate equation time for different cross-linking ratio. RR195 (Dye concentration= 50mg/L, pH 6, T=20°C)

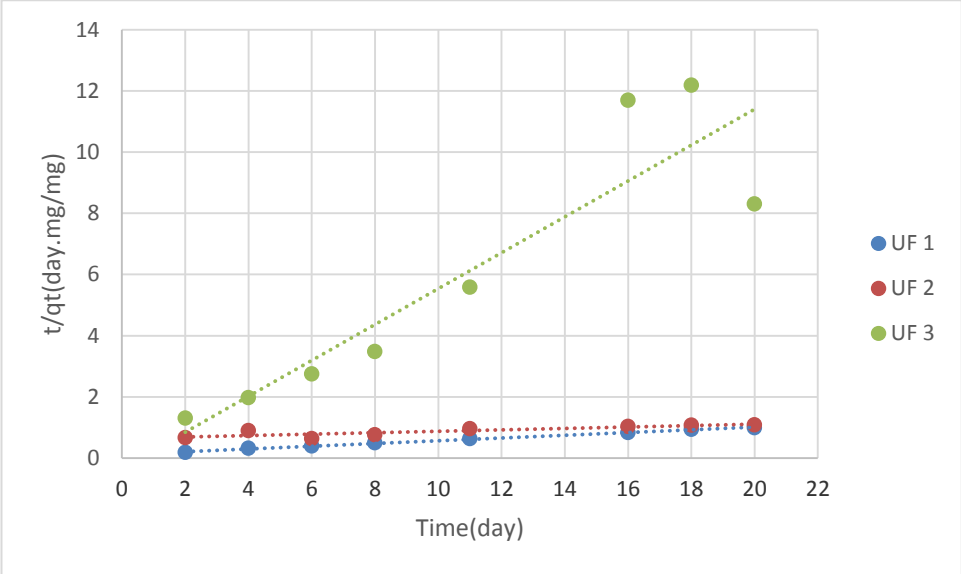


Figure 4.39 : Application of pseudo second order rate equation time for different cross-linking ratio. RR221 (Dye concentration= 50mg/L, pH 6, T=20°C)

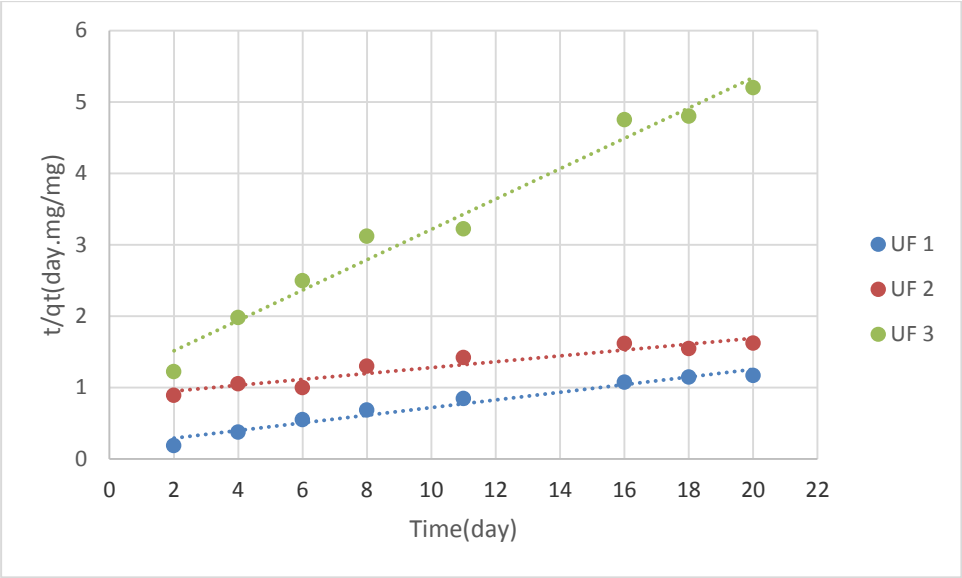


Figure 4.40 : Application of pseudo second order rate equation time for different cross-linking ratio. RB5 (Dye concentration= 50mg/L, pH 6, T=20°C)

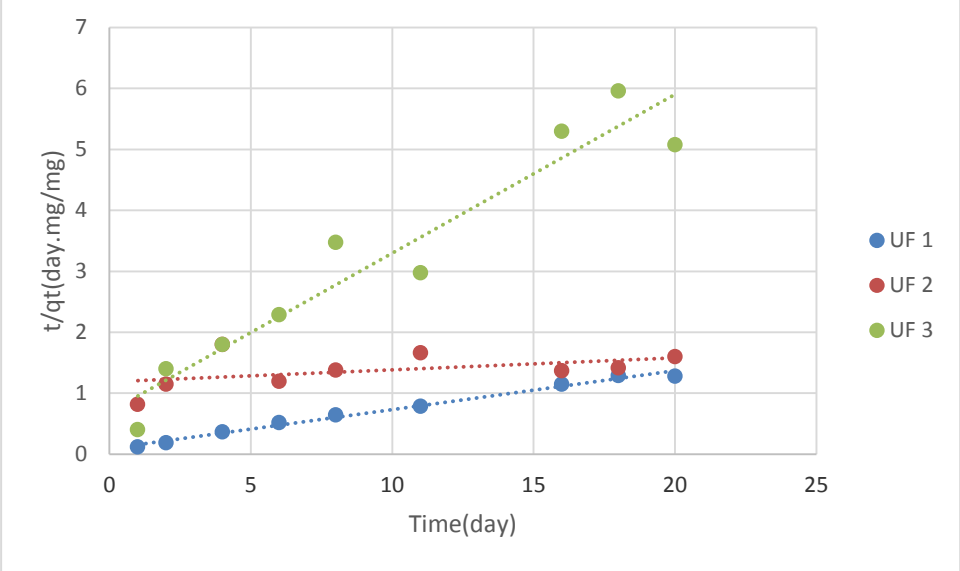


Figure 4.41 : Application of pseudo second order rate equation for different cross-linking ratio. RY145 (Dye concentration= 50mg/L, pH 6, T=20°C)

4.4.5 Comparision of kinetic parameters of chitosan composites in each dye solution

The parameters were found utilizing both pseudo-first order and pseudo-second order rate equations. The results are shown below and compared. Pseudo-second order rate equation was found as the suitable one for adsorption results.

Table 4.1 : Kinetic parameters of chitosan composites for RR195 for different conditions by pseudo-first order rate equation

Reactive Red 195	q_e(mg/mg)	k(day^{-1})	R^2
pH 4	13,12	0,123	0,310
pH 6	5,60	0,075	0,966
pH 8	5,20	0,137	0,961
20°C	14,25	0,153	0,975
35°C	12,60	0,105	0,884
50°C	10,98	0,084	0,903
0.4 (Z/C)	14,98	0,191	0,948
0.8 (Z/C)	9,98	0,180	0,948
UF 1	9,05	0,058	0,943
UF 2	2,96	0,119	0,988
UF 3	18,24	0,266	0,986

Table 4.2 : Kinetic parameters of chitosan composites for RB221 for different conditions by pseudo-first order rate equation

Reactive Blue 221	q_e(mg/mg)	k(day^{-1})	R^2
pH 4	5,79	0,214	0,917
pH 6	70,66	0,512	0,919
pH 8	25,50	0,261	0,973
20°C	35,28	0,396	0,975
35°C	13,15	0,113	0,884
50°C	11,28	0,083	0,847
0.4 (Z/C)	30,71	0,306	0,905
0.8 (Z/C)	13,64	0,288	0,920
UF 1	13,39	0,153	0,986
UF 2	21,64	0,126	0,968
UF 3	0,42	0,020	0,022

Table 4.3 : Kinetic parameters of chitosan composites for RB5 for different conditions by pseudo-first order rate equation

Reactive Black 5	q_e(mg/mg)	k(day^{-1})	R^2
pH 4	4,08	0,153	0,791
pH 6	24,00	0,294	0,966
pH 8	19,88	0,204	0,961
20°C	24,33	0,298	0,975
35°C	15,98	0,252	0,960
50°C	3,35	0,127	0,842
0.4 (Z/C)	22,43	0,265	0,998
0.8 (Z/C)	22,66	0,198	0,998
UF 1	9,46	0,070	0,943
UF 2	21,64	0,108	0,988
UF 3	2,73	0,137	0,986

Table 4.4 : Kinetic parameters of chitosan composites for RY145 for different conditions by pseudo-first order rate equation

Reactive Yellow 145	q_e(mg/mg)	k(day^{-1})	R^2
pH 4	4,95	0,111	0,909
pH 6	16,57	0,218	0,925
pH 8	13,21	0,193	0,956
20°C	28,20	0,318	0,987
35°C	20,32	0,256	0,967
50°C	7,80	0,053	0,993
0.4 (Z/C)	21,96	0,265	0,989
0.8 (Z/C)	9,72	0,129	0,900
UF 1	7,55	0,059	0,861
UF 2	22,41	0,193	0,862
UF 3	2,46	0,193	0,381

By utilizing pseudo-second order rate equation, kinetic parameters (k_2 and q_e) were obtained. According to the tables below, we can have an idea about how adsorption examines in different conditions.

Table 4.5 : Kinetic parameters of chitosan composites for RR195 for different conditions by pseudo-second order rate equation

Reactive Red 195	q_e(mg/mg)	k_2(mg/mg.day)	R^2
pH 4	14,94	0,073	0,983
pH 6	24,03	0,003	0,956
pH 8	17,42	0,002	0,614
20°C	29,94	0,002	0,973
35°C	67,11	0,003	0,963
50°C	14,73	0,004	0,959
0.4 (Z/C)	37,59	0,001	0,935
0.8 (Z/C)	17,10	0,004	0,987
UF 1	17,12	0,021	0,943
UF 2	19,01	0,015	0,988
UF 3	4,61	0,036	0,986

Table 4.6 : Kinetic parameters of chitosan composites for RB221 for different conditions by pseudo-second order rate equation

Reactive Blue 221	q_e(mg/mg)	k_2(mg/mg.day)	R^2
pH 4	16,70	0,070	0,999
pH 6	27,78	0,006	0,970
pH 8	24,75	0,005	0,982
20°C	29,05	0,005	0,981
35°C	25,19	0,004	0,999
50°C	22,94	0,003	0,978
0.4 (Z/C)	34,36	0,003	0,959
0.8 (Z/C)	11,98	0,028	0,977
UF 1	22,42	0,016	0,996
UF 2	37,88	0,001	0,929
UF 3	2,47	0,334	0,988

Table 4.7 : Kinetic parameters of chitosan composites for RB5 for different conditions by pseudo-second order rate equation

Reactive Black 5	q_e(mg/mg)	k_2(mg/mg.day)	R^2
pH 4	15,40	0,113	0,997
pH 6	28,73	0,010	0,993
pH 8	29,06	0,009	0,985
20°C	29,58	0,008	0,945
35°C	21,14	0,020	0,994
50°C	10,23	0,148	0,998
0.4 (Z/C)	28,24	0,010	0,996
0.8 (Z/C)	34,72	0,003	0,980
UF 1	18,66	0,015	0,985
UF 2	24,21	0,002	0,979
UF 3	4,71	0,093	0,975

Table 4.8 : Kinetic parameters of chitosan composites for RY145 for different conditions by pseudo-second order rate equation

Reactive Yellow 145	q_e(mg/mg)	k_2(mg/mg.day)	R^2
pH 4	8,21	0,044	0,968
pH 6	22,57	0,010	0,964
pH 8	20,67	0,016	0,989
20°C	27,62	0,005	0,963
35°C	30,30	0,003	0,959
50°C	16,07	0,002	0,992
0.4 (Z/C)	43,86	0,001	0,975
0.8 (Z/C)	26,60	0,006	0,946
UF 1	15,72	0,042	0,989
UF 2	33,44	0,001	0,985
UF 3	4,02	0,071	0,951

From the tables we can be seen that, different reactive dyes showed similar behaviours for the same composite sample in the same conditions and of course, there are differences related the structures. The best adsorption was obtained at pH 4 for all the samples in the first day, which was at 20 °C. However, after the first day, the adsorption rate slowed down dramatically at pH 4 while it was more constant at pH 6 and pH 8. At the end of the experiments, adsorption capacities were obtained and as you see, pH 6 were the best and it was good to examine the temperature effect since it was easier to control the rate. Adsorption was better at low temperatures,

which showed that the experiments were exothermic although in longer time, at equilibrium, they could have quite interesting results according to adsoption capacities obtained by pseudo-second order rate equation. The increase of clay amount slowed down the adsorprion capacities as shown in the tables, so the amount of the clay used must be optimized for further utilities. UF crosslinking had good effects as medium UF ratio composite increased adsorption capacity for Reactive Blue 221 and Reactive Yellow 145 while high UF ratio composite has highest rate for the adsorption.

5. CONCLUSIONS AND RECOMMENDATIONS

The aim of this thesis was to investigate colour removal of dyes from water with using chitosan-zeolite composites obtained by adsorption method. For this aim, several different composites were prepared by using chitosan and zeolite in different ratios while in some of the cases, urea and formaldehyde were used as crosslinking agent.

Samples were taken from each composite and analyzed by FTIR spectrum and obtained the peaks expected. By SEM, the morphology of the composites were examined in detail. UV/Visible spectroscopy was used to obtain adsorption data. Thus, the changes of adsorption capacities and adsorption rate were examined. Qualitatively, the change of the dye concentration was also sought. In a short time, low temperature, low clay ratio and low pH showed the best characteristics. Cross-linking has also increased adsorption and qualitatively, the material was stronger in acidic solution mediums after crosslinking. In the long time, by considering adsorption capacities and rate constants, they showed a different behavior, which supports pH 6 to be the best adsorption medium. Increase of pH after this value affected negatively.

In conclusion, chitosan/zeolite composite with high crosslinking in gel form showed good adsorption properties and can be used for wastewater treatment in textile industry, which would need adsorption to be fast. It can be recommended that the composite with medium crosslinking ratio may need further study and optimizations for industry since it would be stronger than non-crosslinked composite and may be reused.

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